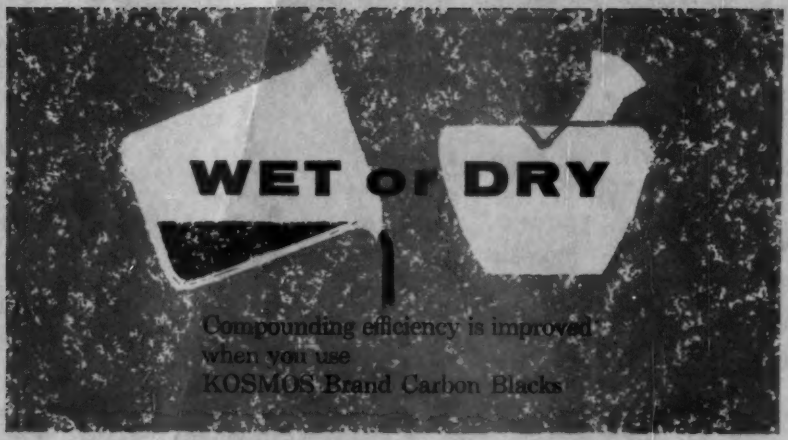
JULY - SEPTEMBER • 1961

VOLUME XXXIV • NUMBER THREE

RUBBER CHEMISTRY AND TECHNOLOGY

PUBLISHED IN FIVE ISSUES BY THE
DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY



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Published in Five Issues (January–March, April–June, July–September, October–November & December) under the Auspices of the Division of Rubber Chemistry of the American Chemical Society, Prince and Lemon Streets, Lancaster, Pa.

Editor.....David Craig
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RUBBER CHEMISTRY AND TECHNOLOGY is published under the supervision of the Editor, representing the Division of Rubber Chemistry of the American Chemical Society. One object of the publication is to render available in convenient form under one cover important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances. Another object is to publish timely reviews.

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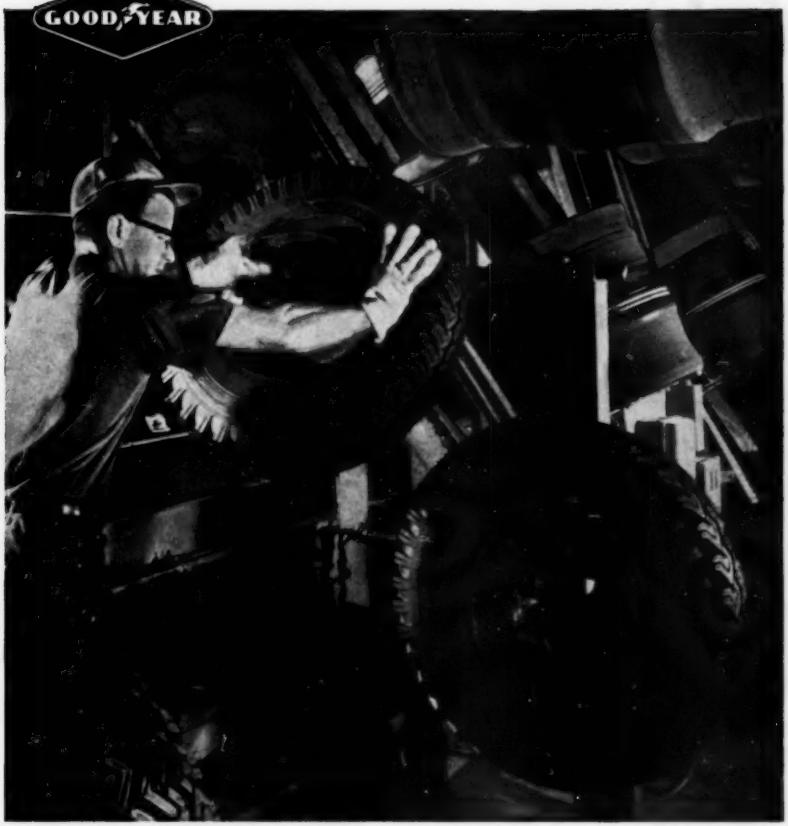

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Shell tears brand-new shoes apart in the search for better footwear, flooring, tires and bottle nipples

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Shell tears new shoes apart

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They then study the sole. Its color. How it adheres to the top. And the most economical way to make each shoe.

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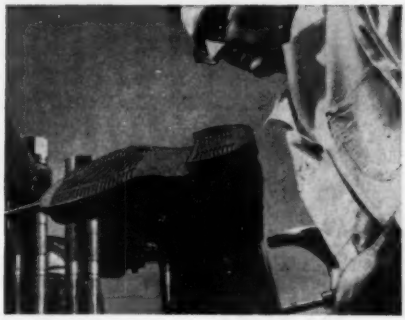

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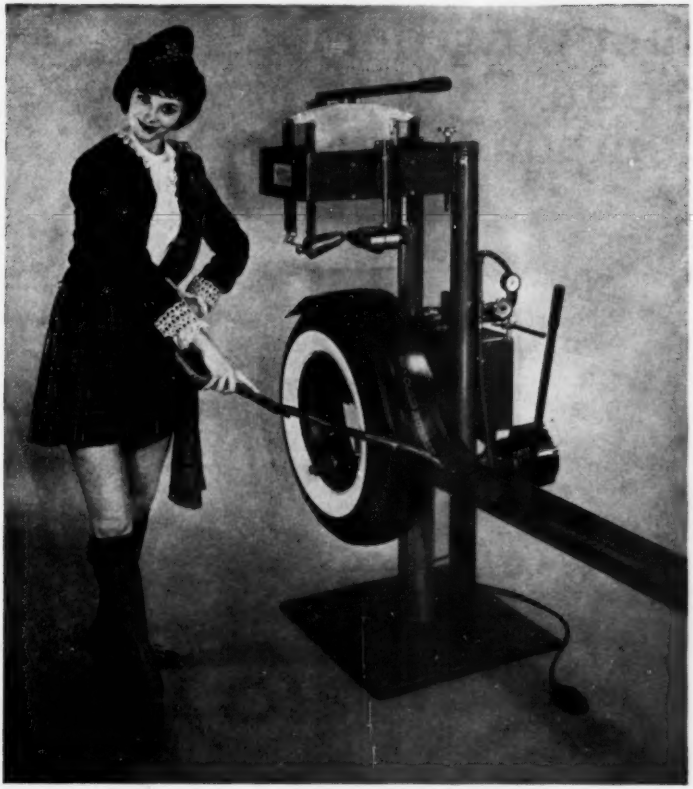

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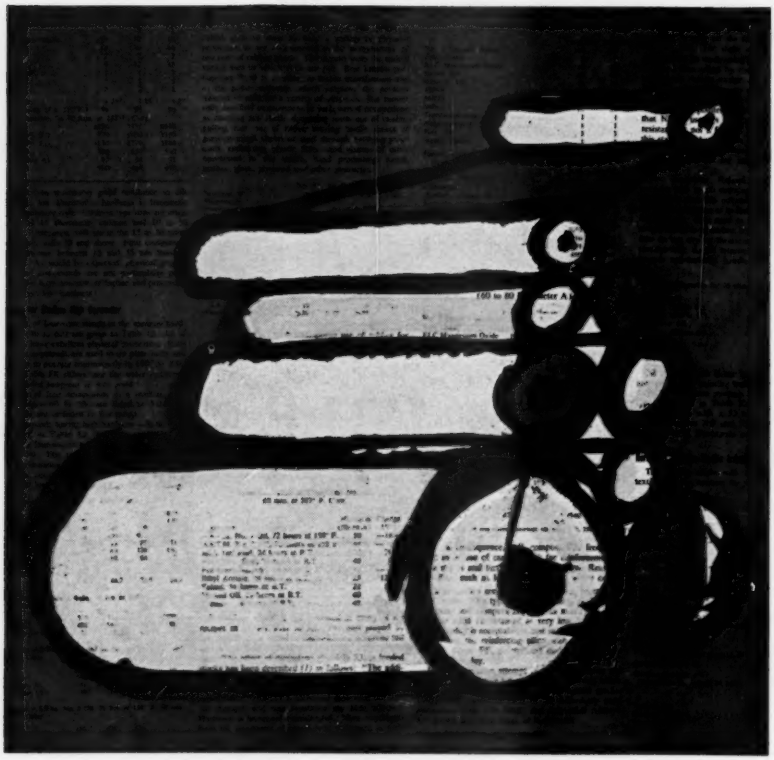
JULY - SEPTEMBER • 1961

VOLUME XXXIV • NUMBER THREE

RUBBER CHEMISTRY AND TECHNOLOGY

PUBLISHED IN FIVE ISSUES BY THE
DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY



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FUTURE MEETINGS

ACS MEETINGS AS OF SEPTEMBER 5, 1961

Meeting	Date	City
Spring 1962	March 20–29	Washington, D. C.
Fall 1962	Sept. 9–14	Atlantic City, N. J.
Jan. 1963	Experimental Third National Meeting	
Spring 1963	Mar. 31–Apr. 5	Los Angeles, Calif.
Fall 1963	Sept. 8–13	New York, N. Y.
Jan. 1964	Experimental Third National Meeting	
Spring 1964	Mar. 31–Apr. 9	Philadelphia, Pa.
Fall 1964	Aug. 30–Sept. 4	Chicago, Ill.
Spring 1965	Mar. 30–Apr. 9	Detroit, Mich.
Fall 1965	Sept. 12–17	Atlantic City, N. J.
Spring 1966	March 22–31	Pittsburgh, Pa.
Fall 1966	Sept. 11–16	New York, N. Y.
Spring 1967		
Fall 1967	Sept. 10–15	Chicago, Ill.
Spring 1968		
Fall 1968	Sept. 8–13 (T)	Atlantic City, N. J.

(T) Tentative.

RUBBER DIVISION MEETINGS

Date		City	Hdqtr. Hotel	Exh. Space
Spring 1962	Apr. 24–27	Boston, Mass.	Statler	—
Fall 1962	Oct. 16–19	Cleveland, O.	Sheraton	Maybe
Spring 1963	May 7–10	Toronto, Canada	Royal York	Yes
Fall 1963	Sept. 10–13	New York, N. Y.	Roosevelt	Maybe
Spring 1964	Apr. 28–May 1	Detroit, Mich.	Cadillac	Yes
Fall 1964	Sept. 1–4	Chicago, Ill.	Sherman	Yes
Spring 1965	May 4–7	Miami Beach, Fla.	Fontainebleau	Yes
Fall 1965	Oct. 19–22	Philadelphia, Pa.	Bellevue-Strat	
Spring 1966	May 3–6	San Francisco, Cal.	Fairmount	Yes
Fall 1966	Sept. 13–16	New York, N. Y.	Roosevelt [1]	
Spring 1967	May 2–5	Montreal, Canada	Queen Elizabeth	Yes
Fall 1967	Sept. 12–15	Chicago, Ill.	Sherman	Yes

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1961

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[1] Tentative.

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Craig, Jr. (Witco Chemical Company, P. O. Box 22443, Houston, Texas). *Meeting Dates* are as follows: Nov. 17–18, 1961, Memphis, Tenn. (Chisca Hotel). Jan. 26–27, 1962, Houston, Texas (Shamrock-Hilton). June 8–9, 1962, Birmingham, Ala. (Dinkler-Tutwiler). Nov. 9–10, 1962, New Orleans, La. (Roosevelt).

Washington Rubber Group

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THE CHEMICAL INSTITUTE OF CANADA RUBBER DIVISION OFFICERS AND SPONSORED RUBBER GROUPS

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977 Aqueduct Street, Montreal, Quebec). *House Committee:* R. W. DICKSON (The Pigment and Chemical Co. Ltd., 6333 Decarie Blvd., Montreal 29, Quebec). *Ladies Night:* L. B. DUNFORD (Northern Electric Co. Ltd., Wire and Cable Division, P. O. Box 6122, Montreal, Quebec). *Sgt. at Arms:* J. R. CLOUTIER (Northern Electric Co. Ltd., Wire and Cable Division, P. O. Box 6122, Montreal, Quebec). *Director at Large:* A. R. OVERING (British Rubber Co. Ltd., 500—20th Ave., Lachine, Quebec).

ELECTION RESULTS—1961

DIVISION OF RUBBER CHEMISTRY, ACS

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NEW BOOKS AND OTHER PUBLICATIONS

AUTOHESION AND ADHESION OF HIGH POLYMERS. S. S. Voyutskiĭ. In Russian. 242 pages; 332 references. Except for one paragraph the *Foreword* by V. A. Kargin and the *Table of Contents*, translated by Earl C. Gregg, Jr., read as follows:

The ability to serve as an adhesive material is one of the most important properties of high polymers. As adhesives high polymers are utilized at the present time for the most diverse purposes, as the adhesive components of aircraft or in rubber goods. Another property of high polymers is their capability of autohesion (self adhesion)—widely used in the technology of processing polymers during the joining of thermoplastics and obtaining molded articles and during the manufacture of films from the dispersions of high polymers, etc.

The monograph of S. S. Voyutskiĭ, (the result) of many years of working on the problems of autohesion and adhesion, represents his own summary of contemporary knowledge in this field. The value of the book lies in the fact that it was written with a single point of view, from the position of the so-called diffusion theory of autohesion and adhesion developed by the author. As is known, this theory, as a result of an examination of the phenomenon of adhesion of high polymers, is based on the most salient features (of the polymer)—chain structure and mobility of the flexible macromolecules which define the possibility of blending polymers in the interfacial layer. As is seen from the monograph, the author justly thinks that his theory is not universal but it envelopes a large part of adhesion and autohesion and the role of it is undoubtedly very great.

In my opinion for all cases of possible mutual blending of polymers this theory, among others, is the most realistic and complete. In this book is found reflection and a different view on autohesion and adhesion of high polymers.

The monograph of S. S. Voyutskiĭ undoubtedly will be helpful for scientific workers, engineers and technicians, all having immediate concern with adhesion as well as being occupied with the general questions of the technology of polymers; the book was written to answer practical questions. It is of indisputable interest to physical chemists working in the field of high polymers because autohesion and adhesion are intimately bound to the structure and properties of the macromolecules of high polymers and also for the creation of a more complex, multicomponent polymeric system.

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TRADE NAMES OF RUBBERS, PLASTICS AND RESINS. Volume 3. Rubber & Plastics Research Association of Great Britain, Shawbury, Shrewsbury, Shropshire, England. 8¼ by 11¾ inches; paper bound; 242 pages. $10. This is the third volume of the RAPRA trade name listing, supplementing Volume 1, published in 1949 and covering the period from 1926 to 1949, and Volume 2, published in 1955 and covering the period from 1949 to 1954. Since this volume supplements Volumes 1 and 2, rather than being a complete list, it is unfortunate that Volume 1 is out of print. A few copies of Volume 2 are available, however, and may be had together with Volume 3 for a combined price of $15. This invaluable volume contains a listing of all registered trade names, plus those for which registration applications have been made, covering, in all, more than 5,500 product listings, with the name of the manufacturer and a brief description of the product. This supplementary list of trade names is about as long as the first one published in 1949, although it covers only five years, compared with 23. It is no wonder, then, that with such a profusion of product names, the listing is an essential reference book. Even for those who have the first two volumes of the listing (and most of us do not), the list would be more valuable if it were brought up to date in one volume, including such information as changes in trade names. Nothwithstanding, this book should be in everyone's library.

[From *Rubber World.*]

A new journal *Soviet Plastics* is now published under the scheme sponsored by the British Department of Scientific and Industrial Research for cover-to-cover translations of important Russian journals. The translation is prepared by Rubber and Plastics Research Association and the journal published by Rubber and Technical Press Ltd., Gaywood House, Great Peter Street, LONDON, S.W. 1., to whom all orders and other correspondence should be

addressed. In "Soviet Plastics" are found articles on the chemistry of plastics, production methods and machinery, the testing of raw materials and finished products, and factory practice. The articles are of a high standard and provide detailed information for the plastics industries of the English-speaking world on the latest achievements of the Soviet Plastics Industry. The new journal is monthly and costs £14 per twelve issues. Each issue will contain approximately 72 pages printed by letterpress.

KAUTSCHUK HANDBUCH. Volume II. Edited by Siegfried Bostrom. Published by Berliner Union G.m.b.H., Stuttgart, Germany. PVC cover, 6¼ by 9 inches; 568 pages; 361 illustrations.

In an irregular order of publication Volume III of Bostrom's four-volume Rubber Handbook, appeared first, followed by Volume I—both reviewed in the November, 1960, issue of Rubber World, (page 48); (also in R. C. & T., January–March, 1960 issue). The material he covers is divided into five parts, and the present Volume II, comprises the final chapters—14 through 18—of Part 1, Volume I, concerned with raw material, as well as Part 2, covering processing techniques and machinery. The raw materials considered in the present volume are: polysulfide rubbers, silicone rubbers, polyurethans and PVC, their preparation, properties, and applications; reclaims of natural rubber, butyl, Perbunan, neoprene, silicones, and Vulkollans receive similar detailed treatment.

Part 2, consists of 11 chapters, of which four give details of the preparation and vulcanizing of compounds of natural rubber; hot and cold butadiene-styrene polymers, blends and stereospecific polymers; butadiene-acrylonitrile copolymers and blends; butyl rubber and latex. The next five chapters take up the use and effects of organic and inorganic compounding ingredients, plasticizers, extenders, pigments and other aids; the preparation and properties of cellulose hydrate fibers, wholly synthetic fibers (polyamide, polyester polypropylene and polyvinyl alcohol); the manufacture, properties, and application of tire cord. The final two chapters are devoted to machinery and auxiliary equipment.

Originally, it had been the intention to devote three chapters in this volume to accelerators, antiagers, and peptizers, respectively, but these could not be prepared in time and will be included in Volume IV. As in the earlier volumes, each chapter in the present book is accompanied by more or less extensive bibliographies. [From *Rubber World.*]

1960 SUPPLEMENT TO BOOK OF ASTM STANDARDS, INCLUDING TENTATIVES. Parts 9 and 10. American Society for Testing Materials, 1916 Race St., Philadelphia, Pa. 9 by 6 inches. Heavy paper covers. $4 per part. (Complete set of supplements is $40.)

The supplements are published annually between triennial publication of the Book of ASTM Standards. Part 9 covers plastics, rubber, electrical insulation, and carbon black, and Part 10 covers textiles, soap, water, atmospheric analysis, and wax polishes.

Those familiar with the Book of ASTM Standards know that it is a very valuable compilation of testing standards. For those unfamiliar with the publication, the 494-page Part 9 includes standards for rubber elastomers, latex, carbon black, sponge, hard rubber, coated fabrics, belting, hose, gaskets, automotive and aeronautical products, 68 standards for plastics, tests for mechanical, thermal, optical, and permanence properties of plastics, plus standards for rubber tapes, ceramics, mica, and other electrical insulating materials.

Part 10, which runs 334 pages, includes standards for fibers, yarns, threads, fabrics, asbestos textiles, cotton, wool and man-made fibers, in addition to soaps, atmospheric analysis, and wax polishes. This book is a must for the technical library. [From *Rubber World.*]

INTRODUCTION TO NATURAL AND SYNTHETIC RUBBERS. D. W. Huke. Cloth; 5¼ × 8¼ inches; 164 pages. Hutchinson & Co., Ltd., London, England. Price 25s.

Here is a book with "introduction to" in its title which is precisely that. There are very few places where it becomes too technical or involved for understanding by a reader not familiar with the rubber industry. In fact, it would be an excellent book for pupils at the high school or college level. It should also find great use in laboratories or plants to introduce the new chemist, engineer, or production supervisor to the field of rubber.

While this reviewer would have to take issue with certain statements or descriptions in the book, it is quite well written and is presented in very logical order. The author, in his final chapter, states that he has the feeling that a great many more things ought to be included: new rubbers, additives, and processes to improve the final product, but that a halt had to be made somewhere. It is unfortunate that he stopped where he did. A continuation including new materials and processes written in this simple clear language would be very useful. It is to be hoped that this will be done in any revision or sequel.

The chapters on history and early developments are very well done and clear. Chapters on processing and compounding are not quite so complete. Major classes of compounding materials are included, but many groups of minor ingredients have been left out. This omission may have been deliberate, but it would appear desirable at least to point out their existence. In processing, the areas of mixing, extruding, calendering, and some molding features are covered adequately. Raw stock preparation, mold and open steam vulcanization, and finishing steps should have been added, or existing sections expanded.

The section on stereo synthetic natural rubbers is particularly weak. There is no indication that these rubbers are in commercial production, and the author passes over polybutadiene as if it were still a lab curiosity.

This book is not a compounding guide, but a general description of natural rubber and most common synthetic rubbers viewed in the light of historical and chemical development with some practical aspects worked into this theme.

[From *Rubber World.*]

INTERNATIONAL RUBBER DIRECTORY. Walter Hirt, Editor. Cloth; 6 by 9 inches; 692 pages. Verlag fur Internationale Wirtschaftsliteratur GmbH., P. O. Box 108, Zurich 47, Switzerland. Price in the United States, $17.00 plus postage (postpaid if remittance accompanies order).

This book is a complete guide to the rubber industry throughout the world. It lists every rubber product manufacturer with his major lines of products and location. There are 72 countries containing rubber companies represented in the book.

The book is divided into five sections. The first section is the listing of product manufacturers. This listing is broken down into continents, countries, and cities within the country. The information includes product line, number of employes, trade marks, brand names, subsidiaries, and affiliated companies.

The second section contains vocabularies of technical terms arranged first in German-English-French, then English-German-French, and finally, French-German-English order. Since the listings in the book may be in any one of the three languages, this section will prove very useful.

The third section is the buyers' guide and contains detailed descriptions for product line and foreign representatives classified both by countries and by product for all suppliers of raw materials to the rubber industry.

The fourth section is a listing of proprietary names used in the industry throughout the world.

The final section is an alphabetical listing of all of the firms contained in the book.

This book should be a very valuable tool for anyone concerned with worldwide rubber industry or any major part of it and is quite interesting even to those whose interest might be academic or personal. [From *Rubber World.*]

RUBBER RED BOOK. Directory of the Rubber Industry Thirteenth edition. M. E. Lerner, Editor. 8¼ × 11¼ inches; 814 pages. Palmerton Publishing Co., New York 1, N. Y. Price, $15.00.

To past users of the previous 12 editions of this directory, little need be said of the value to those in the rubber industry that this publication affords. In general, this edition is similar in make-up and content with the preceding edition. There are some minor changes which should prove beneficial. All suppliers to the industry are listed in one place this time rather than being scattered throughout the material sections. In addition, sales offices and phone numbers have been included where known, for extra convenience.

In the mind of this reviewer, the large size and the paper cover are still detrimental to the most valuable use of this book. The cover stock weight has been increased this year, but is still not sturdy enough for a book which may receive considerable use during the year. In many places, copies are passed on to subordinates or associates at the end of the year and a torn copy with damage to the index loses some of its usefulness. The large size makes it very difficult to keep the book in a handy place on the desk where a reference book of this type is most useful.

In balance, however, it is quite well done, and there is little question but what many people have been waiting for this delayed annual edition to appear. [From *Rubber World.*]

PREPARATIVE METHODS OF POLYMER CHEMISTRY. By Wayne Sorenson and Tod W. Campbell. Published by Interscience Publishers, Inc., 250 Fifth Ave., New York 1, N. Y. 6¼ × 9¼ in.; 337 pp. $10.50.

This book is a compilation of detailed procedures for the laboratory synthesis and handling of numerous types of polymers. It is designed both as a reference work and as a supplementary text for laboratory courses in polymer chemistry or advanced organic synthesis. The authors report that this type of reference work has been previously unavailable, and in making their assembly have relied on widely-scattered sources, including technical journals and patents. Where original literature did not contain sufficient data, additional material based on their own experience or that of their colleagues has been added. The authors are, respectively, research chemist and research manager at DuPont's Pioneering Research Division of the Textile Fibers Department.

The procedures assembled here have been divided into five basic types, con-

taining most of the known classes of polymers and organic polymer-forming reactions. As defined, "polymer" is a substance of sufficiently high molecular weight, such that the properties have become reproducibly fixed. Among selections they have included are many familiar plastics and synthetic rubbers. The five basic categories used are: polycondensation and hydrogen transfer polymerization; addition polymers from unsaturated monomers; ring opening polymerization; non-classical routes to polymers, and synthetic resins.

Specific procedures, worthy of mention to those involved in synthetic rubber chemistry, are contained in the series on addition polymerization. Among them: butadiene, styrene-butadiene copolymers, butadiene-acrylonitrile copolymers, isoprene (as polymerized with *n*-butyl lithium, finely divided lithium and with a titanium-based catalyst), styrene-isoprene; isobutylene-isoprene, and chloroprene.

The book is well-documented with original sources of the preparations given in each instance. Drawings and illustrations used in the introductory chapter, on preparation, fabrication and characterization of polymers, are adequate.

[From *Rubber Age.*]

RUBBER AND RAILWAYS IN THE NINETEENTH CENTURY. P. L. Payne. Cloth; 5¾ by 8¾ inches; 216 pages. Liverpool University Press, Bedford House, 75 Bedford St. South, Liverpool 7, England. Price, 30 s.

Essentially this work on the firm of George Spencer & Co., which merged with the firm of Stephen Moulton & Co. in 1891, is a companion volume to an earlier work published by Liverpool University Press, a history of the Moulton company titled, "The Rise of the British Rubber Industry during the Nineteenth Century."

George Spencer devised new rubber springing systems, vacuum hoses, valves, washers, window seals for use on British railways, had the parts made to his specifications by rubber producers and ironmasters, assembled the parts, and sold them to the railways. In a large sense he was one of the first of the modern manufacturing middlemen.

Mr. Payne, Colqhoun Lecturer in business history at the University of Glasgow, has done a definitive study on George Spencer & Co., based on the Spencer papers, a collection of patent specifications, legal agreements, patent specifications, and letters to and from parts manufacturers, agents, salesmen, consulting engineers, and railway officials. Although basically for the specialist in rubber industry history, "Rubber and Railways in the Nineteenth Century" casts considerable light on the problems of a British manufacturer in the last half of the Nineteenth Century. [From *Rubber World.*]

POLYMERIC MATERIALS. By Charles C. Winding and Gordon D. Hiatt. Published by McGraw-Hill Book Co., 330 W. 42nd St., New York 36, N. Y. 6¼ × 9¼ in.; 406 pp. $12.00.

Polymers are the primary materials in the plastics, rubber, protective coating and textile fiber industries. Although these four industries developed separately and even today have separate sales and technical service forces where single companies overlap them, the authors have seen a need for a text which is unified, and covers the common denominator of them all. Their working assumption is that "For an engineer or scientist, a broad general background in polymeric materials, not restricted by industries, is desirable regardless of specific employment."

In this context, then, they have provided an introductory volume which concentrates on the chemical, physical and engineering aspects of polymers.

The success of the volume is accordingly dependent on the clarity and organization and scope and depth of the material selected. Fortunately, both authors have used substantial portions of the manuscript as lecture notes in introductory courses on polymeric materials for several years prior to publication date. They report that students have readily accepted the order of presentation of material which they have incorporated here. This involves an initial introduction to the chemistry of polymers, including molecular structure and properties. This is followed by applications and fabrication methods. The first part thus covers fundamentals that are common to many polymers; the second contains detailed discussions of specific commercial polymers.

By way of general comment, it should be mentioned that charts, tables and listings are exceedingly clear and straightforward. Typography is good.

A listing of the specific chapters follows: (1) Polymer Structure and Polymerization Reactions (2) Solutions and Molecular Weights of Polymers (3) General Properties of Plastics (4) and (5) General Applications of Polymeric Materials (6) Natural Products and Their Derivatives (7) Polymers Formed by Condensation Reactions (8) Ethenic Polymers (9) Silicones (10) Rubbers.

References, pertaining to works in the four specific fields, are included at the end of each of the chapters. [From *Rubber Age.*]

The *ASTM Bulletin* is changed to *Materials Research* and *Standards* and is appearing in 1961 as Vol. 1.

79th MEETING DIVISION OF RUBBER CHEMISTRY ACS

BROWN HOTEL, LOUISVILLE, KENTUCKY

April 19–21, 1961

MEETING HIGHLIGHTS

1. Dr. Herbert E. Winkelmann was the 1961 Charles Goodyear Medalist, and the medal was presented to him at the Banquet.
2. An excellent lecture was given at the Meeting by Dean Henry Eyring of the University of Utah. (Page 32.)
3. Mr. Robert L. Murray and Mr. J. Donald Detenber of the E. I. du Pont de Nemours Company were the recipients of the Best Paper Award for their paper, "A Study of First- and Second-Order Transitions in Neoprene," which was presented at the New York Fall Meeting in September, 1960. (Page 33.)
4. A number of items that were voted and approved by the Executive Committee are as follows:
   a. There will be no banquet in Cleveland for the Fall Meeting of 1962. (Page 32.)
   b. The Division of Rubber Chemistry Library can sell photostats of papers presented at National Meetings. (Page 12.)
   c. A bylaw change should be written and obtained in which the Business Manager instead of the Editor of R. C. & T. prepares the budget for R. C. & T.
   d. Bylaw changes involving the three-year term for Directors, deleting the Auditing Committee, and deleting a reinstatement charge for members and associate members late on dues payment are to be sent to Washington for approval.
   e. The Business Manager of R. C. & T. should handle subscriptions instead of the Treasurer.
   f. The mailing list is to be changed from Lancaster Press to Crawford Letter Company, and this latter concern is to handle dues collection.
   g. A voucher system is to be used in which the Treasurer makes out a voucher for each bill and has it signed by the Chairman or Vice-Chairman before payment.
   h. The Division is to sponsor a flight to Europe next spring to cover the Fourth Rubber Technology Conference in London, May 22 to 25, 1962. The Chairman is to appoint a Committee to handle this.
   i. For the Best Paper Award, papers should be judged on both quality of presentation and scientific content.
5. A number of assignments are as follows:
   a. The Future Meetings Committee is to report on future meeting hotels that have exhibit space, one and one-half years prior to the meeting.

b. The Membership Committee is to make a recommendation at the next meeting as to whether there should be a differential in dues between United States membership and Mexican and Canadian membership.
c. The Nominating Committee is to get the cost of separate mailing of ballots and biographies and give a recommendation as to whether this should be done. Also, it is to make a specific recommendation on a bylaw change on petition balloting.
d. The Library Policy Committee is to make a recommendation at the next meeting concerning what can be done about Dr. H. J. Osterhoff's proposal that the Division of Rubber Chemistry sponsor "Machine Searching of Rubber and Plastics Literature."
e. The Treasurer is to make a definite recommendation at the next meeting on a place to handle the sale of past volumes of RUBBER CHEMISTRY AND TECHNOLOGY.

Emeritus Members

G. H. BRITTAIN
SEWARD BYAM
R. D. GARTRELL
W. E. GLANCY (New)
F. L. HOLBROOK (New)
C. D. KENNEDY
FREDERICK MARCHIONA
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Necrology

ELMER I. RAMGA
August 28, 1960
CARL A. BARTLE
September 29, 1960
NEWMAN W. HESS
October 4, 1960
GEORGE L. ALLISON
October 26, 1960
CHARLES R. HAYNES
November 21, 1960
JONAS KAMLET
December 16, 1960
KENNETH C. CROUSE, SR.
January 5, 1961
C. A. HEMINGWAY
January 23, 1961
HARRY L. FISHER
March 19, 1961
J. D. GAFFEN
March 25, 1961

Best Paper Committee, Chairman Harold Tucker

Mr. Tucker reported that the paper, "A Study of First- and Second-Order Transitions in Neoprene" by Robert M. Murray and J. Donald Detenber, Elastomers Laboratory, Elastomer Chemicals Department, E. I. du Pont de Nemours and Company, was selected to receive the award for the best paper presented before the Division of Rubber Chemistry at the 138th Meeting of the ACS in New York, September 14–16, 1960.

It was reported that a revised rating sheet is being used for the Division Meeting in Louisville, April 18–21, 1961. It was voted and approved by the Committee that for the Best Paper Award, the papers should be rated on both the quality of the presentation and the quality of the scientific content.

Bibliography Committee, Chairman J. McGavack

Mr. M. E. Lerner reported that the Bibliography for 1955–56 has been distributed; the one for 1957–58 will be ready in six months, and that the one

for 1959 would be completed between the end of the year or early 1962. It was reported that we should show a profit on the Bibliography when we get it on an annual basis.

TECHNICAL PROGRAM OF THE 79TH MEETING

1—Introductory Remarks. W. S. Coe, *Chairman.*

2—Thermodynamic and Transport Properties of Monomers and Polymers. Henry Eyring (University of Utah, Salt Lake City, Utah). (Invited Paper.)

3—The Structure of Various Natural Rubbers. F. W. Stavely, J. L. Binder, P. H. Biddison, M. J. Forster and H. G. Dawson (Firestone Tire and Rubber Co., Akron, Ohio). (Paper presented by Mr. Dawson.)

4—Biaxial Fatigue Testing of Vulcanizates. S. D. Gehman, P. Rohall and D. I. Livingston (Goodyear Tire and Rubber Co., Akron, Ohio). (Paper presented by Mr. Gehman.)

5—Analysis of the Force-depth Relation in the Penetration of Rubber Compounds. G. S. Yeh and D. I. Livingston (Goodyear Tire and Rubber Co., Akron, Ohio). (Paper presented by Mr. Yeh.)

6—The Measurement of Structure in Carbon Blacks. Andries Voet, William N. Whitten, Jr. and Archie C. Teter (J. M. Huber Corp., Borger, Texas). (Paper presented by Mr. Voet.)

7—The Analysis of Pigment Dispersion in Rubber by Means of Light Microscopy, Microradiography and Electron Microscopy. William M. Hess (Columbian Carbon Co., Princeton, N. J.).

8—A Study of Ozone Resistance of Neoprene Vulcanizates. Peter Katsenis and E. G. Partridge (TLARGI Rubber Technology Foundation, University of Southern California, Los Angeles, Calif.). (Paper presented by Mr. Katsenis.)

9—Protection of Neoprene Latex Films Against Discoloration by Light. R. O. Becker and R. L. Seligman (E. I. duPont de Nemours & Co., Wilmington, Del.). (Paper presented by Mr. Becker.)

10—Protection of Neoprene Vulcanizates Against Heat Aging. K. L. Seligman and P. A. Roussel (E. I. duPont de Nemours & Co., Wilmington, Del.). (Paper presented by Mr. Seligman.)

11—Differences Between Butadiene-Acrylonitrile Copolymer Blends and Single Copolymers. Carl E. Fleming (B. F. Goodrich Chemical Co., Avon Lake, Ohio).

12—Swelling Effects of Liquids on Nitrile Rubbers. Phillip H. Starmer and Carl H. Lufter (B. F. Goodrich Chemical Co., Avon Lake, Ohio). (Paper presented by Mr. Starmer.)

13—Development and Application of a High Solids Nitrile Rubber Latex. J. M. Mitchell, G. K. Watson and H. L. Williams (Polymer Corp., Sarnia, Ont., Canada). (Paper presented by Mr. Mitchell.)

14—Coatings for Rubber. H. A. Winkelmann (Dryden Rubber, Chicago, Ill.). (Charles Goodyear Medal Lecture.)

15—Urethan and Urethan-Urea Elastomers Prepared by a One-Shot Method. S. L. Axelrood, C. W. Hamilton and K. C. Frisch (Wyandotte Chemicals Corp., Wyandotte, Mich.). (Paper presented by Mr. Axelrood.)

16—New Techniques in Processing Urethan Elastomers. K. A. Pigott, J. W. Britain, William Archer, B. F. Frye, R. J. Cote and J. H. Saunders

(Mobay Chemical Co., New Martinsville, W. Va.). (Paper presented by Mr. Pigott.)

17—Machine Literature Searching with the IBM-101. LEORA E. STRAKA (Goodyear Tire & Rubber Co., Akron, Ohio).

18—Injection Molding of Silicone Rubber. ROBERT P. DESIENO (General Electric Co., Waterford, N. Y.) and ROBERT FUHRMAN (Lewis Welding and Engineering Co., Cleveland, Ohio). (Paper presented by Mr. DeSieno.)

19—Determination of Nonylphenyl Phosphite in SBR Latex and Polymer by a Direct UV Spectrophotometric Method. HEINZ J. BRANDT (U. S. Rubber Co., Naugatuck, Conn.).

20—Antioxidant Efficiency of *p*-Phenylenediamines in Natural Rubber Vulcanizates. O. LORENZ and C. R. PARKS (Goodyear Tire and Rubber Co., Akron, Ohio). (Paper presented by Mr. Lorenz.)

21—The Static U-Adhesion and Dynamic Strip Adhesion Methods for Tire Cord Adhesion Testing, W. H. NICOL and D. D. RAY (Goodyear Tire & Rubber Co., Akron, Ohio). (Paper presented by Mr. Ray.)

22—Some New Interpretations of the Tire Cord Fatigue Phenomenon. W. G. KLEIN, W. J. HAMBURGER and M. M. PLATT (Fabric Research Laboratories, Inc., Dedham, Mass.). (Paper presented by Mr. Klein.)

23—Tubeless Tire Performance Related to Inner Liner Properties. R. H. DUDLEY and J. V. FUSCO (Enjay Laboratories, Linden, N. J.). (Paper presented by Mr. Dudley.)

THE CHEMISTRY OF CARBON BLACK IN RUBBER REINFORCEMENT *

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INTRODUCTION

It is generally recognized that the three primary properties of carbon black involved in the reinforcement of rubber are particle size or surface, structure, and surface chemistry. Electron microscope investigations in the early 1940's provided the means for rationalizing the reinforcement contributions of particle size and structure. The role of carbon surface chemistry on the other hand, while extensively studied, has to a large extent remained unsolved.

Wiegand and Snyder[1] in 1938 studied the acidic and basic properties of carbon black by pH measurements and correlated pH with cure rate as shown in Figure 1. This was one of the first attempts to rationalize the effect of carbon black surface chemistry on rubber reinforcement and the studies indicated that the chemistry of the carbon particle could play a significant role in the behavior of carbon-rubber compounds. Since then the bulk of the work in this area has been directed to the identification of the oxygen-containing groups on the carbon surface.

Villars[2] measured active hydrogen by the Grignard reagent and determined that about 26% of the total oxygen reacted with the methyl magnesium iodide Grignard reagent and from the quantity of methane evolved concluded that of this amount of reactive oxygen about 14% is bonded to an active hydrogen. Smith and Schaeffer[3] observed a number of oxygen containing groups in the electronically excited emission spectra of carbon black. Studebaker[4], using the reaction of carbon black with diazomethane as his criterion, reported the presence of hydroxyl and carboxyl groups on the carbon black and also suggested the possibility of 1,4-quinone groups being present. More recently Hallum[5] demonstrated by polarographic and infrared spectroscopic methods the presence of hydroxyl and quinone groups on the surface of carbon black. Garten and coworkers[6] after extensive study concluded that the functional groups primarily responsible for chemical interaction with rubber were f-lactone groups on acidic carbons and chromene groups on basic carbon blacks.

In contrast to the extensive investigations on the chemical nature of the oxygen functional groups on the carbon black surface, the chemistry of the underlying carbon surface itself has received relatively little attention. This lack of interest is understandable in the case of channel black where the amount of surface oxygen is sufficient to form a mono-layer over the whole surface. Whether or not such a layer actually exists is of course not known. A major portion at least of the channel carbon surface is covered with oxygen atoms chemically combined in one way or another with the carbon. In the case of furnace carbons, with smaller amounts of surface oxygen, the nature of the

* Presented at the 78th Meeting of Division of Rubber Chemistry, ACS, NewYork, September, 1960.

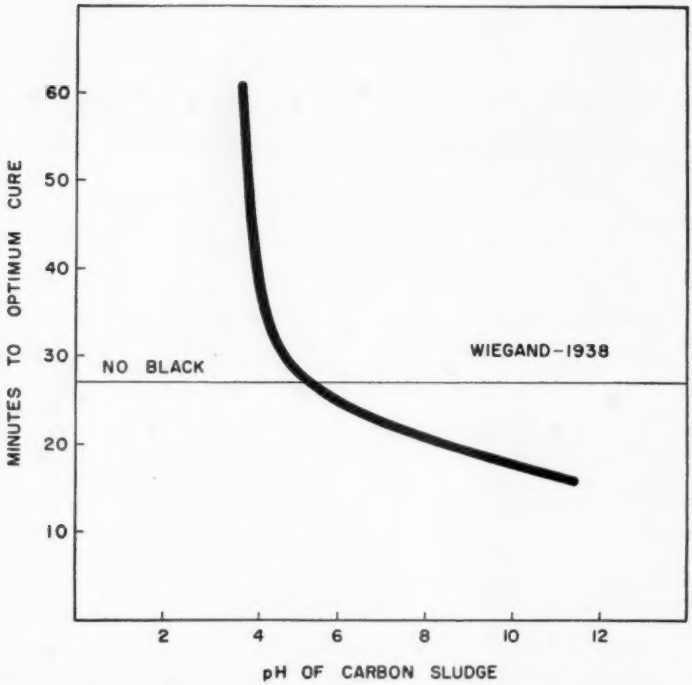

FIG. 1.—pH of carbon vs. optimum cure for a natural rubber—DPG compound.

LOSS OF CHEMISORBED OXYGEN AND CRYSTALLITE REARRANGEMENT BY HEAT TREATMENT OF CARBON BLACK
– SCHEMATIC –

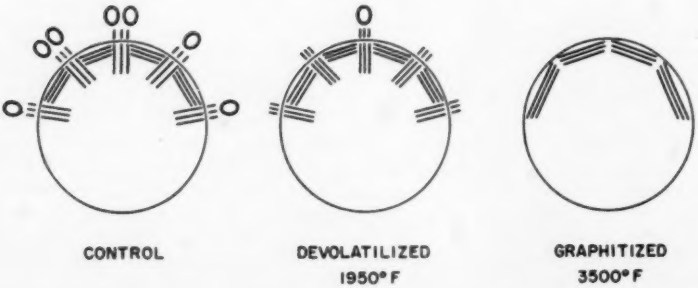

FIG. 2.

carbon surface itself would be expected to play a relatively more important role. Such surface active carbon could arise from the nature of the aromatic polynuclear structures comprising the surface layer. Such structures are relatively active, especially in complexing reactions, some of the bonds in polynuclear aromatics exhibiting a relatively high degree of bond order. In addition, the presence of unpaired electrons in carbon black has been shown by Collins et al.,[7] and their influence on rubber properties, particularly modulus, has been demonstrated by Kraus and Collins[8] and Watson and Jervis[9].

The purpose of the present paper is to probe further into the role of oxygen functional groups and carbon surface activity, with the emphasis on the effects produced in the reinforcement of rubber rather than on the analysis of surface details. This might be termed a macro approach to the problem as opposed to the micro approach.

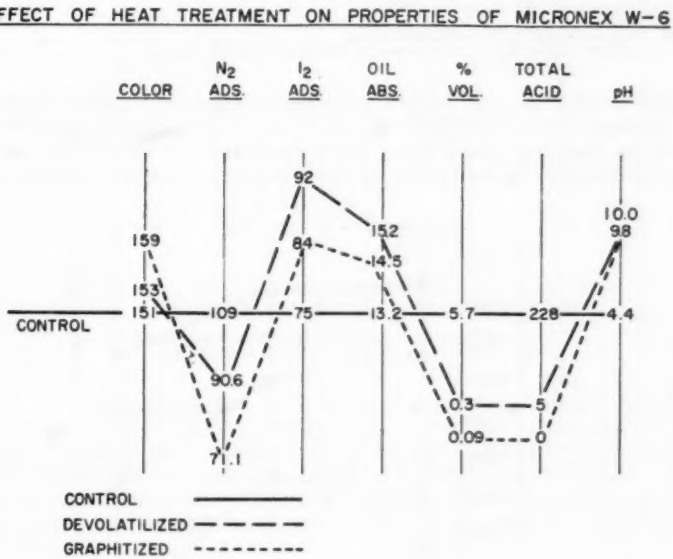

Fig. 3.

EXPERIMENTAL

To follow this approach a series of treated carbon blacks were prepared to provide a wide variety of single variable changes in the quantity and type of surface chemistry on two standard tread carbons, EPC and ISAF. For convenience in testing and discussion these carbons are placed in two groups according to the primary treating process employed, removal of chemisorbed oxygen and the addition of chemisorbed oxygen.

Removal of Chemisorbed Oxygen.—The carbon blacks employed were Micronex W-6 and Statex 125 representing the EPC and ISAF grades, respectively. Chemisorbed oxygen was removed by heat treating under a nitrogen atmosphere at 1950° F for two hours. This *devolatilization* treatment

TABLE I

PROPERTIES OF HEAT TREATED CARBONS

Carbon	Statex 125			Micronex W-6		
Heat treatment	None	Devolatilized	Graphitized	None	Devolatilized	Graphitized
Properties						
Color	140	141	146	151	153	159
Tinting strength	116	114	101	107	106	101
Oil absorption[1]	13.6	15.8	14.2	13.2	15.2	14.5
N_2 adsorption[2]	107	114	94	109	90	71
I_2 adsorption	104	119	100	75	92	84
% Volatile	2.0	0.4	0.05	5.7	0.3	0.09
pH	7.2	9.9	10.0	4.4	9.8	10.0
Total acid[3]	72	2	0	228	5	0
Ionized acid	1	−11	−2	2	−15	−1

[1] Stiff Paste-Ball End Point-gallon/100 lb.
[2] BET-m^2/g.
[3] Equivalents NaOH $\times 10^6$ neutralized/gram.
[4] Equivalents Acid or Base $\times 10^6$ released on treatment with NaCl/gram.

is sufficient to remove all oxygen from channel black, but higher temperatures are necessary for the complete removal of oxygen from furnace blacks[10]. This condition, together with a likely slight reoxidation of the carbon surface at room temperature before testing, results in a residue of oxygen on carbon blacks

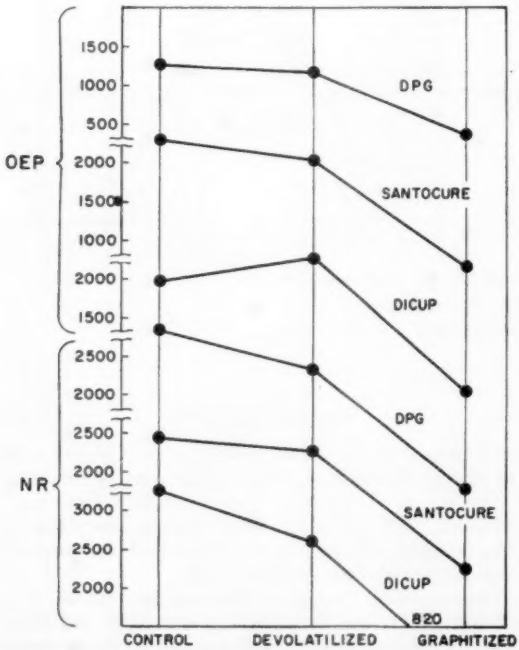

FIG. 4.—Effect of heat treatment of Statex 125 on 40'L-300 in 2 polymers with 3 curing systems.

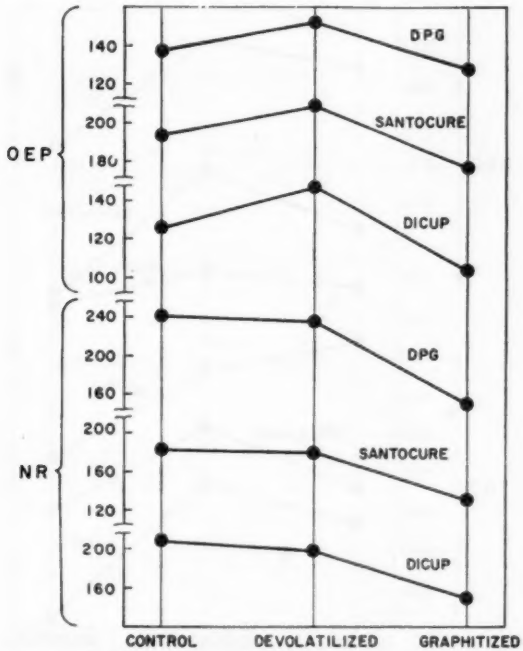

FIG. 5.—Effect of heat treatment of Statex 125 on crosslink density in 2 polymers with 3 curing systems at 60′cure.

treated in the foregoing manner. The treatment is known, however, to have little effect upon the crystallite arrangement of the carbon black and so the basic carbon black surface structure is left unchanged. The state of the carbon black particle after devolatilization is presented schematically in Figure 2. An intermediate devolatilization, by treating the carbon for two hours at 1400° F, was also applied to the ISAF carbon and the effects produced were included in several studies.

Both carbons were also partially graphitized by heat treating in a nitrogen atmosphere at 3500° F for two hours. This treatment removed any residual oxygen functional groups and also rearranged the surface crystallites. The crystallite rearrangement was indicated by X-ray diffraction patterns which showed the general sharpening of the absorption bands and the occurrence of the 004 band typical of the graphitization process. The electron microscope also showed the change from a spherical to a polyhedral appearance characteristic of graphitized carbon black. This change in the crystallite structure of the carbon black particle is also shown schematically in Figure 2.

The specific changes in the chemical and physical properties accompanying these two treatments are tabulated in Table I and graphed in Figure 3. The tinctorial, absorption and adsorption results show that surface area and structure are relatively unaffected by the treatments. Electron microscope examination of the treated carbons revealed no change in particle diameter. The

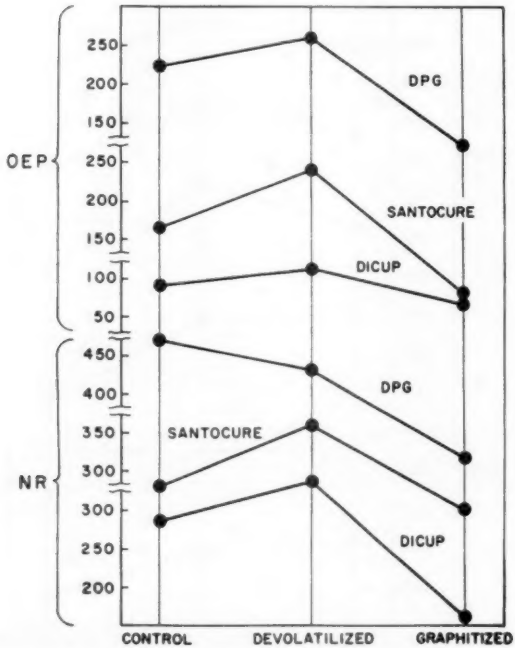

FIG. 6.—Effect of heat treatment of Statex 125 on hot tear (212° F) in 2 polymers with 3 curing systems.

loss in percentage oxygen volatile, essentially complete for the graphitized carbons, is reflected in decreased total acid and increased pH.

Effect of removal of chemisorbed oxygen on rubber properties.—The heat treated carbons, control, devolatilized and graphitized, representing successive steps in the removal of functional group and carbon surface chemistry, were tested in the two polymers and three curing systems shown below.

	Recipes					
	SBR-1710			Natural rubber		
	1	2	3	1	2	3
Rubber	100	100	100	100	100	100
Carbon black	50	50	50	50	50	50
Zinc oxide	3	3	—	3	3	—
Stearic acid	2	2	—	2	2	—
DPG	4	—	—	2	—	—
Santocure[1]	—	1	—	—	0.4	—
Sulfur	2	2	—	2.5	2.5	—
Dicup[2]	—	—	3	—	—	3

[1] N-Cyclohexyl-1,2-benzthiazolyl sulfenamide (Monsanto).
[2] Dicumyl peroxide (Hercules).

TABLE II

RUBBER PROPERTIES OF HEAT TREATED STATEX 125 CARBONS IN SBR-1710 WITH 3 RECIPES

Recipe	DPG			Santocure*			Dicup		
Treatment	None	Devol.	Graph.	None	Devol.	Graph.	None	Devol.	Graph.
Vulcanized properties (cured at 293° F)									
Optimum cure[1]	40′	37′	37′	25′	25′	27′	25′	23′	23′
20′ L-300	690	660	260	1090	1170	240	860	1130	300
20′ Tensile	2230	2520	2240	2920	3140	2640	2260	2680	2010
90′ L-300	1970	1740	480	2660	2350	720	—	—	880
90′ L-500	—	—	1430	—	—	2140	—	—	—
90′ Tensile	3340	3180	2810	3360	3320	3100	2670	2510	1970
90′ Elong.	445	480	670	365	390	570	275	255	455
90′ S.H.	58	57	50	63	62	54	59	62	51
Log R	4.3	2.5	2.2	3.7	2.2	1.8	3.8	2.4	1.9
Rebound	51.0	43.7	37.4	53.9	48.7	42.4	60.5	57.9	46.9
Dispersion (visual)[2]	8.0	7.8	7.3	8.0	8.3	7.5	8.0	7.8	7.5
Dispersion (mic.)[3]	99	99	98	99	99	99	98	98	97
Crescent tear[4]	215	260	122	166	242	80	88	108	68
De Mattia flex[5]	3.2	3.8	3.8	3.2	3.8	6.8	2.5	2.1	3.8
Crosslink density[6]	138	152	127	194	208	177	126	147	104
Unvulcanized properties									
Mooney visc.[7]	56.0	60.0	62.5	—	—	—	59.5	62.0	63.0
Mooney scorch[8]									
5 Units	4.3	3.7	3.0	10.5	10.1	9.2	3.1	2.0	2.0
35 Units	7.6	6.5	5.2	12.4	12.2	13.7	5.1	3.5	3.2
Carbon gel[9]	33	31	—	34	31	15	29	31	13

[1] Estimated from scorch and stress-strain results.
[2] Rating on torn surface.
[3] % below .9 microns.
[4] Tested at 212° F, at 100% overcure (lbs/in).
[5] KC to 50% failure (pierced groove) at room temp.
[6] $\times 10^6$, moles/cc.
[7] ML-4-212° F.
[8] ML-293° F.
[9] % insoluble rubber.
* Overcure stress-strain data at 60′ in Santocure series.

TABLE III

RUBBER PROPERTIES OF HEAT TREATED STATEX 125 CARBONS IN NATURAL RUBBER WITH 3 RECIPES

Recipe	DPG			Santocure			Dicup		
Treatment	None	Devol.	Graph.	None	Devol.	Graph.	None	Devol.	Graph.
Vulcanized properties (cured at 293° F)									
Optimum cure[1]	15′	15′	15′	20′	20′	23′	20′	20′	18′
10′ L-300	1670	1480	480	1510	1440	460	1080	980	370
10′ Tensile	3560	3590	2610	2960	3600	2340	1790	2120	1970
45′ L-300	2930	2400	790	2460	2270	730	—	2760	890
45′ L-500	—	—	2400	—	—	2100	—	—	2860
45′ Tensile	4030	4090	3410	3820	4100	3420	3260	3700	2910
45′ Elong.	450	485	605	430	495	635	285	365	505
45′ S.H.	66	64	62	64	63	61	61	60	56
Log R	3.1	2.1	2.0	3.3	2.1	1.8	3.6	2.3	2.0
Rebound	68.4	64.6	61.5	67.3	65.1	61.0	70.7	69.0	65.1
Dispersion (visual)[2]	6.0	8.0	8.0	6.5	8.5	8.0	4.8	7.5	8.5
Dispersion (mic.)[3]	85	98	98	85	96	99	85	96	99
Crescent tear[4]	468	418	318	280	360	247	284	339	132
De Mattia flex[5]	8.4	8.3	7.1	43.7	100.1	7.9	6.6	57.0	3.2
Crosslink density[6]	242	235	150	151	175	127	209	198	140
Unvulcanized properties									
Mooney vis.[7]	78.0	78.0	69.0	—	—	—	77.5	2.0	89.5
Mooney scorch[8]									
5 Units	2.8	2.0	1.3	4.9	4.7	5.5	2.6	2.1	1.5
35 Units	3.6	2.7	3.5	5.8	5.8	7.9	3.4	2.9	2.2
Carbon gel[9]	52	51	35	59	52	44	48	49	36

[1] Estimated from scorch and stress-strain results.
[2] Rating on torn surface.
[3] % below 9 microns.
[4] Tested at 212° F. at 100% overcure (lbs/in).
[5] KC to 50% failure (pierced groove) at room temp.
[6] $\times 10^4$, moles/cc.
[7] ML-4-212° F.
[8] ML-293° F.
[9] % insoluble rubber.

The selection of these three curing systems, DPG-sulfur, Santocure-sulfur and Dicumyl peroxide as the crosslinking agents, was made for two reasons. First there was the increasing body of evidence that a large part of the reinforcing action of carbon black occurs during the vulcanization step, both by direct reaction with the polymer[11] and by interaction with the curatives. Secondly, the recent evidence that the curing reaction may proceed by a polar, a mixed polar-free radical or a completely free radical mechanism[12], made it desirable to study the effect of carbon black surface chemistry on the vulcanization reaction as a function of the type of curing reaction. These three curing

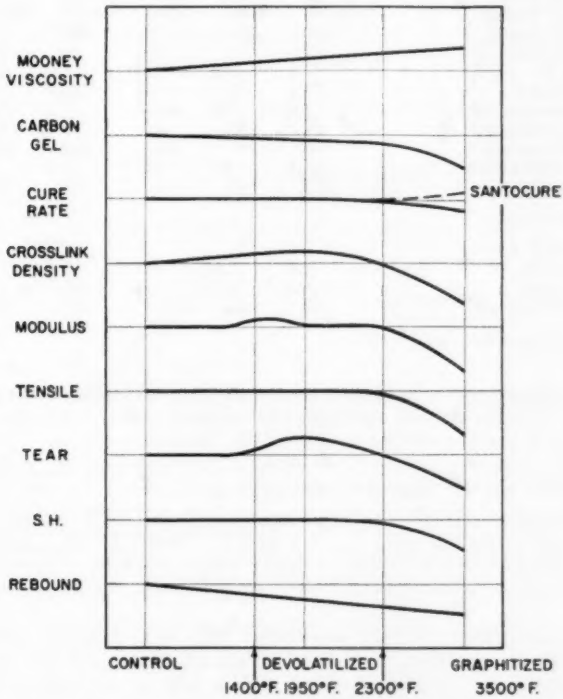

FIG. 7.—Effect of heat treatment of Statex 125 on properties in NR and OEP with DPG, Santocure and Dicup.

systems were accordingly chosen following the Shelton and McDonel evidence, as being representative of a polar, a mixed polar-free radical and a pure free radical mechanism.

Test results for the heat treated ISAF (Statex 125) carbons in SBR-1710 with the three curative systems are given in Table II. The corresponding results in Natural Rubber are presented in Table III. Results for the Channel EPC (Micronex W-6) carbons in both polymers with the Santocure recipe are set forth in Table IV. Significant data from these tables are graphed in Figures 4 to 6.

TABLE IV

RUBBER PROPERTIES OF HEAT TREATED MICRONEX W-6 IN NR AND SBR-1710 WITH SANTOCURE RECIPE

	NR			SBR-1710*		
Treatment	None	Devol.	Graph.	None	Devol.	Graph.
Vulcanized properties (cured at 293° F)						
Optimum cure	35′	30′	40′	30′	20′	25′
10′ L-300	800	1240	220	200	980	160
10′Tensile	1790	3710	1060	1000	3060	1810
45′ L-300	1730	1860	540	1480	1760	500
45′ L-500	3640	3680	1670	3020	—	1490
45′ Tensile	3640	4160	3600	3260	2940	3000
45′ Elong.	500	550	690	525	430	635
45′ S.H.	59	61	58	59	59	50
Log R	7.9	2.5	1.8	7.5	2.6	1.9
Rebound	70.7	67.3	61.5	53.9	49.6	42.8
Dispersion visual	7.0	5.5	8.3	7.3	6.8	7.3
Dispersion mic.	98	85	95	99	97	98
Crescent tear	246	297	184	188	182	93
De Mattia flex	38.1	8.4	7.7	2.6	5.3	4.1
Crosslink density	151	175	127	176	199	165
Unvulcanized properties						
Mooney scorch						
5 Units	6.8	4.0	6.6	13.6	8.3	10.6
35 Units	8.5	5.2	9.3	17.7	10.8	15.3
% Carbon gel	59	52	44	29	24	13

* Vulcanized properties at 20′ and 60′ cures.

In all curing systems in both polymers the heat treatment steps apparently have little effect on time to optimum cure although a slight retarding action is observed with the graphitized carbon in the Santocure system. In fact there was no indication of a carbon black-curative interaction in any of the curative systems based on the observed vulcanizate properties. In view of this conclusion the general effects in all curative systems are presented graphically in Figure 7. It is apparent that no major loss in reinforcement potential develops in Statex 125 with almost complete loss of surface oxygen. The large changes take place only after the crystallite growth and rearrangement process sets in.

Those properties generally associated with the chemical interaction of carbon black and elastomers, such as carbon gel content of the unvulcanized stock, modulus and crosslink density, either show no decrease or only slight increases when chemisorbed oxygen is removed from the surface with no material alteration of the underlying carbon structure. Tear strength is definitely improved in all curative systems. The intermediate 1400° F treatment produced a slight but significant modulus increase. These findings are not in accord with those of previous investigators[13] who showed a steady decrease in these properties with removal of surface oxygen.

Rebound resilience does however drop as surface oxygen is removed and drops further as the carbon surface becomes graphic. It is possible that rebound, in measuring the mechanical hysteresis which primarily occurs at the carbon-rubber interface, is more sensitive to bond strength and that these bonds which replace oxygen linkages on the devolatilized surface are somewhat weaker.

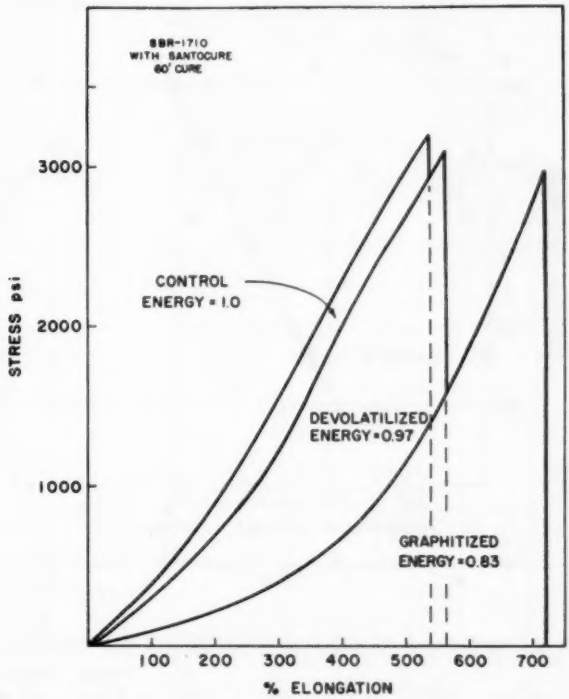

FIG. 8.—Effect of heat treatment of Statex 125 on energy of rupture (control = 1.0).

The results for Micronex W-6 given in Table IV show modulus produced by the devolatilized Micronex to increase. At least part of this increase is undoubtedly due to the well known effect of surface oxygen upon sulfur cure.

Previous data concerning this point are conflicting. Two reports[13, 14] stated that channel black modulus decreases, whereas another[15] claims that modulus increases after a similar treatment. It is probable that, apart from the cure effect, a slight modulus increase is produced with the removal of oxygen from channel black as is the case with furnace black. Increased chemical activity, arising perhaps from increased unpaired electron concentrations, may be responsible.

The effect of the drastic heat treatment, which leads to partial graphitization, on modulus is, however, well defined as previously observed. This drop in modulus for the graphitized black leads to a significant decrease of rupture energy as determined by the area under the stress-strain curve (Figure 8). Road testing of SBR-1710 treads compounded with these three blacks gave the results presented in Figure 9. These wear results show a striking correlation with the energy of rupture. Again, a relatively small effect is produced both upon rupture energy and road wear by devolatilizing. Only when the carbon surface itself is altered is a marked effect produced. The wear performance of the graphitized black, at 65% of control, which checks well with previous

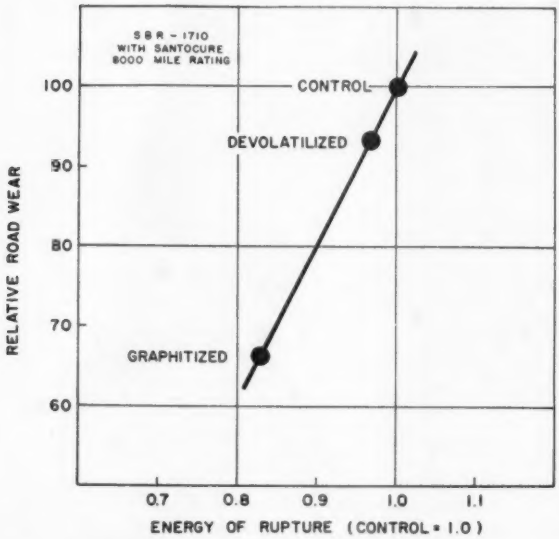

Fig. 9.—Effect of heat treatment of Statex 125 on energyof rupture vs. road wear.

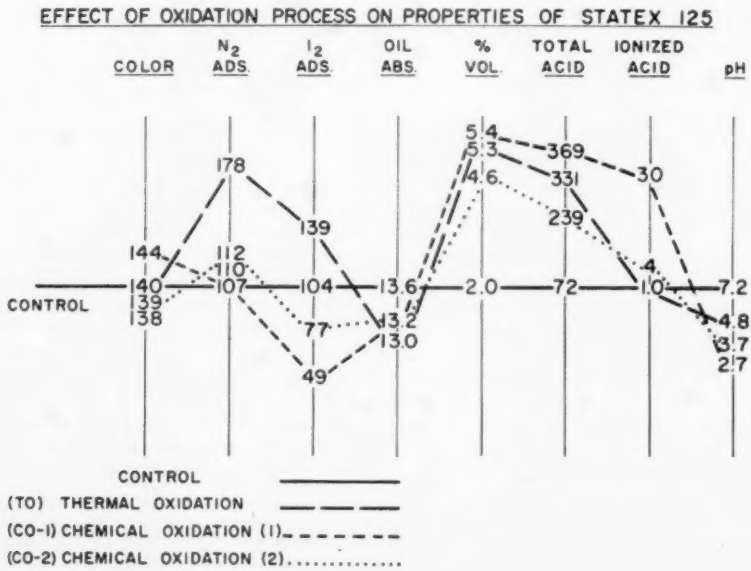

Fig. 10.

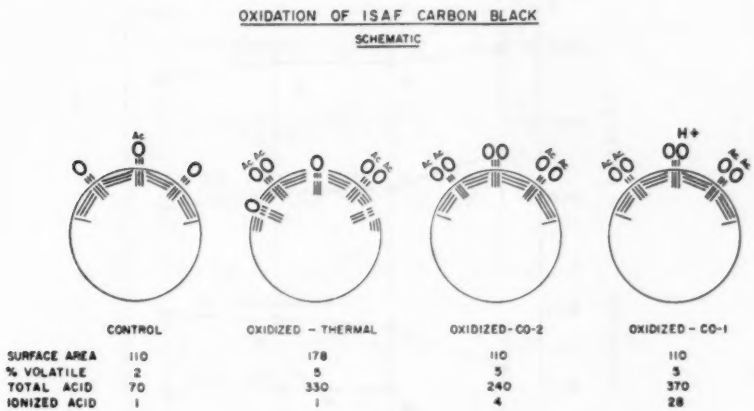

Fig. 11.

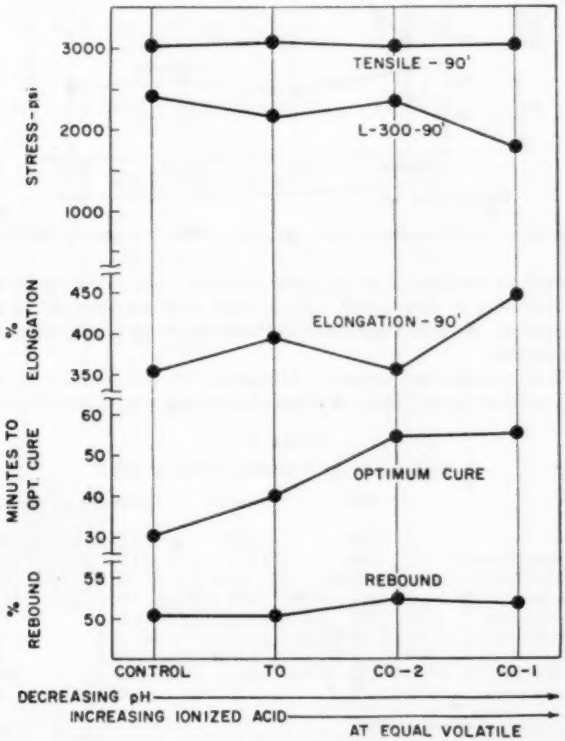

Fig. 12.—Effect of oxidation treatment of Statex 125 on vulcanizate properties in SBR-1710 with Santocure.

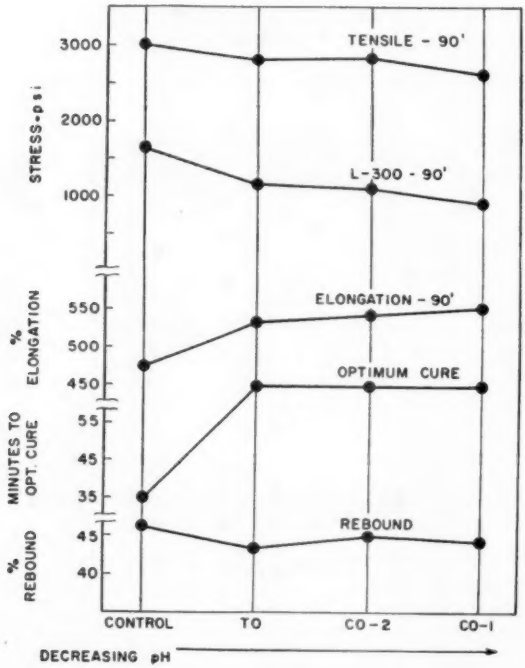

FIG. 13.—Effect of oxidation treatment of Statex 125 on vulcanizate properties in SBR-1710 with DPG.

findings[13] must be attributed to physical bonding only since chemical bonding has been completely eliminated. It is this combination of physical and chemical bonding that distinguishes carbon black as a superior reinforcing pigment in rubber.

Addition of chemisorbed oxygen.—Oxidation of the surface of Statex 125 (ISAF) was carried out by three methods in order to develop differences in the

TABLE V

PROPERTIES OF OXIDIZED STATEX 125

Oxidation Properties	None	Thermal	Chemical-1	Chemical-2
Color	140	139	144	138
Tinting strength	116	112	116	114
Oil absorption[1]	13.6	13.0	13.2	13.2
N_2 adsorption[2]	107	178	110	112
I_2 adsorption	104	139	49	77
% Volatile	2.0	5.3	5.4	4.6
pH	7.2	4.8	2.7	3.7
Total acid[3]	72	331	369	239
Ionized acid	1	1	28	4

[1] Stiff paste-ball end point-gallon/100 lb.
[2] BET-m^2/g.
[3] Equivalents NaOH $\times 10^6$ neutralized/gram.
[4] Equivalents acid or base $\times 10^6$ released on treatment with NaCl/gram.

TABLE VI

RUBBER PROPERTIES OF OXIDIZED STATEX 125 CARBONS IN SBR-1710 WITH 3 RECIPES

Recipe	DPG				Santocure				Dicup			
Oxidation	None	Thermal	Chem-1	Chem-2	None	Thermal	Chem-1	Chem-2	None	Thermal	Chem-1	Chem-2
Vulcanized properties (cured at 293° F)												
Optimum cure[1]	35′	60′	60′	60′	30′	40′	55′	55′	25′	25′	30′	30′
20′ L-300	450	120	90	120	1025	350	50	70	900	670	725	600
20′ Tensile	2280	650	530	590	2560	1350	325	440	2250	2100	1930	1950
90′ L-300	1620	1175	960	1125	2430	2190	1800	2350	—	2150	1800	1820
90′ L-500	—	2540	2200	2480	—	—	—	—	—	—	—	—
90′ Tensile	3000	2830	2660	2850	3040	3100	3080	3050	2440	2520	2630	2620
90′ Elong.	475	535	550	545	355	395	445	365	250	340	390	400
90′ S.H.	61	59	59	60	65	63	62	66	61	57	56	56
Log R	3.2	3.2	4.9	3.9	3.0	3.2	5.1	3.7	3.1	2.8	5.2	4.0
Rebound	46.4	43.7	45.1	44.6	50.6	50.1	52.0	52.5	59.5	56.9	57.9	58.4
Dispersion (visual)[2]	7.5	8.0	7.5	7.5	7.5	7.8	7.8	7.8	7.0	7.5	6.8	6.8
Dispersion (mic.)[3]	99	99	99	99	99	99	97	99	98	97	97	97
Crescent tear[4]	199	210	205	199	185	201	172	138	48	82	92	99
De Mattia flex[5]	3.6	4.5	6.5	5.2	1.8	2.9	3.0	1.3	1	2.5	8.7	8.8
Crosslink density[6]	129	111	90	98	196	174	138	165	137	117	109	107
Unvulcanized properties												
Mooney visc.[7]	57.5	60.0	65.0	60.0	62.5	64.0	6.70	64.0	68.0	66.0	75.0	69.0
Mooney scorch[8]												
5 Units	4.0	6.9	6.7	6.6	8.9	11.8	11.5	12.3	3.0	2.8	2.6	2.3
35 Units	6.7	13.8	14.7	13.5	10.8	15.4	17.8	17.9	4.2	4.3	4.4	4.4
Carbon Gel[9]	28	29	28	27	31	31	29	31	34	30	32	31

[1] Estimated from scorch and stress-strain results.
[2] Rating on torn surface.
[3] % Below 9 microns.
[4] Tested at 212° F, at 100% overcure (lbs/in.).
[5] KC to 50% failure (pierced groove) at room temp.
[6] $\times 10^6$, moles/cc.
[7] ML-4-212° F.
[8] ML-293° F.
[9] % insoluble rubber.

kind of oxygen functional groups at the same total combined oxygen level. These differences in kind of groups should, it was felt, bring out differences in the nature of the interaction with the polymer provided the type of oxygen functional groups was a significant factor.

The first oxidation treatment was carried out by thermally heating the carbon in air at a temperature of 750° F for 1½ hours. The two chemical oxidations were carried out at room temperature under conditions required to add substantially the same amount of oxygen to the carbon surface as the thermal treatment.

The effects of these treatments on the physical and chemical properties of the black are shown in Table V and Figure 10. The tinctorial, absorption and adsorption results indicate little change in the surface area and structure of the chemically oxidized carbon although thermal oxidation significantly increased the area. Again, particle diameter, as estimated by electron microscope examination, was unchanged. The properties associated with added oxygen were, however, changed significantly. At substantially the same oxygen volatile level these treatments developed significant differences in the pH, total acid and ionized acid, indicating unquestionably marked differences in the nature of the oxygen functional groups. A schematic picture of the variations in the make-up of these groups is presented in Figure 11.

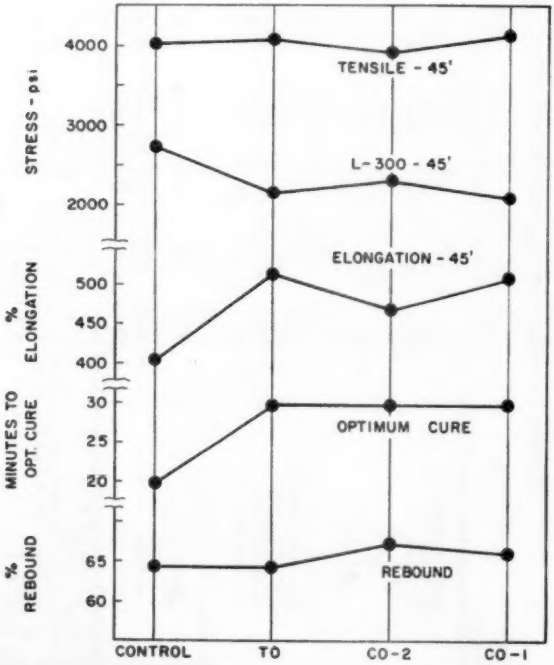

FIG. 14.—Effect of oxidation treatment of Statex 125 on vulcanizate properties in NR with DPG.

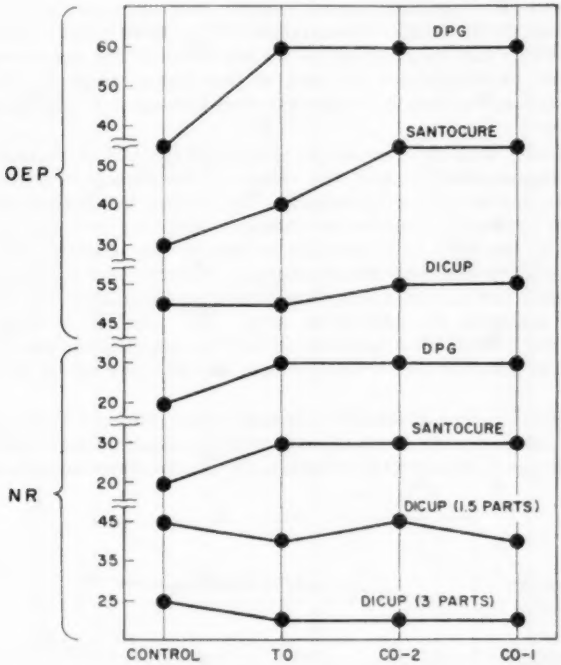

FIG. 15.—Effect of oxidation treatment of Statex 125 on time to optimum cure in 2 polymers with 3 curing systems.

The thermal treatment and the CO-2 treatment developed oxygen groups of essentially the same type. Total acid was increased on both over that in the control. ("Ac" in Figure 11 indicates an acidic oxygen functional group.) The only difference lies in the increased porosity indicated for the thermal treatment. The CO-1 treatment produced both more acidic oxygen groups as well as much more ionizable hydrogen than the other two treatments.

Effects of added chemisorbed oxygen on rubber properties.—This series of oxidized carbons was also tested in two polymers (SBR-1710 and natural rubber) with the same curative systems (DPG-sulfur, Santocure-sulfur and Dicup), with the summarized results of SBR-1710 given in Table VI and the more significant results presented graphically in Figures 12, 13, 14, 15, 16.

It is apparent that except for the expected retardation of cure rate for the DPG and Santocure recipes caused by the oxidized blacks, only minor changes in vulcanizate properties were produced by the differences in the type of oxidation. Results in the dicumyl peroxide system, in which vulcanization has been stated to proceed by a free radical mechanism, differed in several respects from those in the other two systems. This was especially true of cure rate and modulus. None of the oxidation treatments had any effect upon cure rate in the natural rubber dicumyl peroxide system, although as expected a decisive effect was produced on cure rate in the sulfur systems. A smaller effect was produced in the SBR-1710 peroxide cure.

This result has several implications: first, some confirmation is given to the polar mechanism of sulfur vulcanization. The more polar surface of the oxidized carbons can be regarded as an ion trap, in the same sense as the quinones and hydroquinones are used as free radical traps by Shelton and McDonel, and act to terminate the reaction through ion adsorption on the carbon surface.

Concurrently with the increase in polarity of the carbon surface produced by adding chemisorbed oxygen, the ability of the carbon to adsorb and inactivate free radicals is also increased. This ability has been observed both directly and indirectly in numerous instances and may account for the cure retardation of the SBR-1710 peroxide system by the oxidized carbon. The lack of retardation observed in the natural rubber-peroxide system may result from increased free radical adsorption during mastication which partially or completely saturates the adsorption sites. The presence of different antioxidants in the SBR-1710 and natural rubber is a complicating factor, especially marked in the peroxide cure system, which may alter the action of the carbon black.

The oxidized carbon black-peroxide interaction observed in natural rubber and SBR-1710 cure rate is also found with crosslink density and modulus. These effects are in the expected direction, i.e. in natural rubber-peroxide cures.

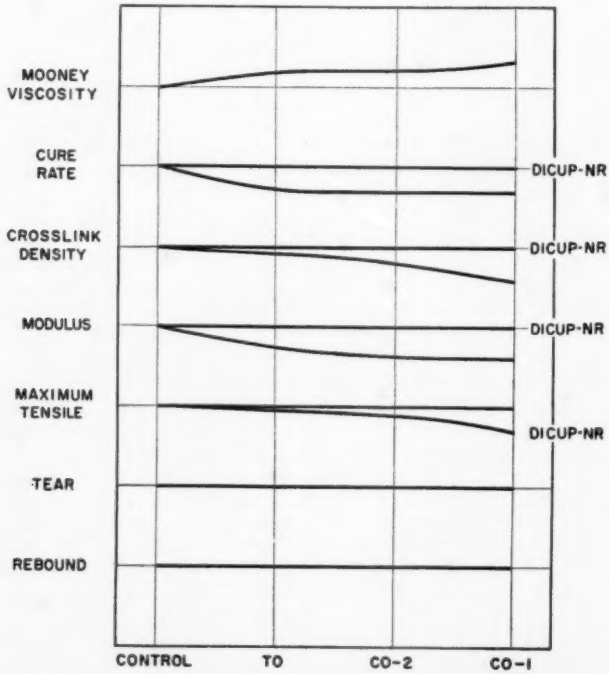

FIG. 16.—Effect of oxidation treatment of Statex 125 on properties in NR and OEP with DPG, Santocure and Dicup.

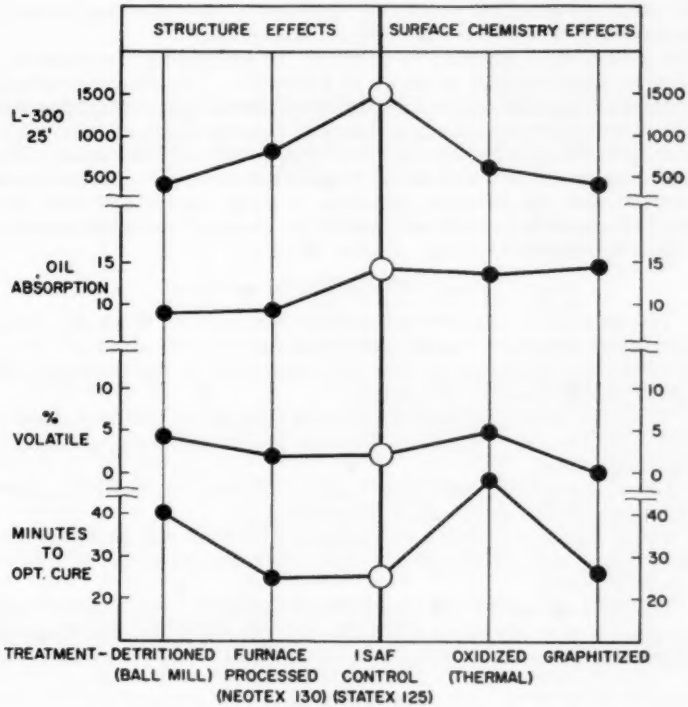

FIG. 17.—Role of structure and surface chemistry on modulus of ISAF carbon, fineness and surface area constant.

Crosslink density is unaffected by added oxygen while the level falls off for the other combinations. The same is true for modulus. In both cases, the effect is slightly greater for the CO-1 treatment which produces a generally more polar surface. The slightly decreased tensile produced by the oxidized carbon in the natural rubber peroxide curative system is associated with a reduced degree of carbon dispersion.

Modulus via structure and surface chemistry effects.—It has been shown in the preceding sections of the paper that modulus is reduced drastically by graphitization, due to destruction of all oxygen functional groups as well as the underlying surface chemical activity. In spite of the normal structure level, modulus is also drastically reduced by added oxygen which affects cure. The role of structure in modulus development is obviously dependent upon the presence of normal surface chemical activity.

Furnace carbons of normal surface chemical activity with lowered structure have been developed recently in the HAF, ISAF and SAF ranges of fineness, the Columbian grades identified as Neotex 100, Neotex 130 and Neotex 150, respectively. Typical properties of Neotex 130 are shown in Figure 17. It is noted that with volatile and cure rate substantially equivalent to that for

Statex 125, the Neotex 130 develops a significantly lower modulus due entirely to the structure reduction indicated by oil absorption.

The mechanical breakdown of structure, by ball milling for example, will also lead to lower modulus as shown in Figure 17. This structure reduction, however, is accompanied by an increase in volatile, with a resultant decrease in the rate of cure, the combined effect of the two factors being to decrease modulus to levels lower than can be accounted for by structure reduction alone. Figure 17 demonstrates the two approaches to modulus control at constant fineness and surface area, via structure reduction at equal volatile and cure, or via chemical effects such as increased volatile or destroyed chemical activity at equivalent structure.

CONCLUSIONS

1. The removal of chemisorbed oxygen from channel black and furnace black, without alteration of the underlying carbon surface, results in only minor effects in reinforcement potential regardless of the curative system employed, whether polar or free radical.

2. When the underlying carbon surface is changed by heat treatment to a state of lower energy, a significant decrease in the reinforcing ability of the carbon black results.

3. Different types of oxygen functional groups added to the carbon surface produce similar effects upon rubber properties.

4. These effects are limited to retardation of cure rate in sulfur curing systems. Only small effects of any kind are produced in the natural rubber-peroxide system.

5. The net conclusion to be drawn is that combined oxygen on the carbon surface plays a relatively minor role in the chemical effect of carbon black upon reinforcement; the nature of the carbon surface itself is of primary importance.

REFERENCES

[1] Wiegand, W. B. and Snyder, J. W., *Proc. Rubber Tech. Conf.* 484 (1938).
[2] Villars, D. S., *J. Am. Chem. Soc.* **70**, 3655 (1948).
[3] Smith, W. R. and Schaeffer, W. D., *Proc. Second Rubber Tech. Conf.* 403 (1948).
[4] Studebaker, M. L., et al., *Ind. Eng. Chem.* **48**, 162 (1956).
[5] Hallum, J. V. and Drushel, H. V., *J. Phys. Chem.* **62**, 110 (1958).
[6] Garten, V. A. and Weiss, D. E., *Ind. Chemist.* **35**, 525 (1959).
[7] Collins, R. L., Bell, M. D. and Kraus, G., *J. Appl. Phys.* **30**, 56 (1959).
[8] Kraus, G. and Collins, R. L., *Rubber World* **139**, 219 (1958).
[9] Watson, J. W. and Jervis, R., *Kautschuk u. Gummi* **12**, WT11 (1959).
[10] Unpublished work, Columbian Carbon Company (1956).
[11] Berry, J. P. and Cayre, P. J., *J. App. Polymer Sci.* **3**, 213 (1960)
[12] Shelton, J. R. and McDonel, E. T., *Proc. Int. Rub. Conf.*, Washington, Nov. 1959, p. 596.
[13] Schaeffer, E. D. and Smith, W. R., *Ind. Eng. Chem.* **47**, 1286 (1955).
[14] Watson, J. W., *Trans. Inst. Rubber Ind.* 2L, 204 (1956).
[15] Snow, C. W., Paper presented at Southern Rubber Group Meeting, Feb. 21, 1958.

PEROXIDE AND RADIATION CURED COMPOUNDS FILLED WITH REINFORCING FINE PARTICLE SILICA *

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INTRODUCTION

A hydrated fine particle silica, Hi-Sil 233, has particle dimensions characteristic of a fully reinforcing filler[1, 2] and undergoes chemical filler-polymer interactions similar to a typical HAF carbon black (Philblack 0)[3]. Initial evidence for ability to undergo filler-polymer interactions appears in the formation of filler-polymer gel (bound rubber) during the mixing or heating of simple filler-elastomer mixtures. Data have been presented which show that, similar to the HAF black, the fine particle reinforcing silica forms significant amounts of bound rubber by a process which is substantially chemical and proceeds by a free radical mechanism[3]. A mechanism by which reactive polymer chain fragments can be accepted for crosslinking purposes by reinforcing fillers of dissimilar surface chemistry has been proposed[3].

Although the fine particle silica reinforces common elastomers crosslinked by the usual sulfur vulcanizing systems, its high potential suggested by bound rubber behavior remains to be fully realized. A valid measure of the degree to which the reinforcing potential of a filler is developed is the value of the ratio η/η_0, the crosslink density of the cured, filled compound divided by the crosslink density of the similarly cured, unfilled control. For Hi-Sil 233 filled-SBR and Hevea vulcanizates, the value of this ratio seldom exceeds one[1] at practical loadings, despite the combination of over 85% of the sulfur[4, 5].

Vulcanization by means of dicumyl peroxide or radiation leads to ideal model systems for study of the η/η_0 ratio. Crosslinking is reported to proceed in each for both filled and unfilled mixtures by a relatively uncomplicated free radical mechanism[6–8]. Also, the use of such curing systems permits the association of any filler-polymer activity more directly with bound rubber development occurring by a free radical mechanism.

EXPERIMENTAL

Natural rubber used in this study was No. 1 ribbed smoked sheet. The reinforcing fillers were fine particle reinforcing silicas made by Columbia-Southern Chemical Corp., Hi-Sil 101 (no longer produced) and Hi-Sil 233, and a high-abrasion furnace (HAF) carbon black, Philblack 0, made by Phillips Petroleum Co. Other curing ingredients were common rubber grade products obtained from a variety of sources. The filler and rubber were mixed in an

* Reprinted from the *J. appl. Polym. Sci.* 5, 397 (1961). Presented before the Division of Rubber Chemistry, ACS, September, 1960. The present address of J. B. Bachmann is Department of Chemistry, The University of Akron, Akron, Ohio.

TABLE I

FORMULATIONS FOR RADIATION CURE

	A-R	B-R	C-R	D-R	E-R	F-R
No. 1-RSS	100	100	100	100	100	100
Antioxidant[a]	—	2	—	—	2	—
Hi-Sil 233	—	—	29.3	58.5	58.5	—
Philblack 0	—	—	—	—	—	54.0

[a] Antioxidant 2246 (American Cyanamid), 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol).

internal mixer (Banbury, size B). In the peroxide study, dicumyl peroxide was added on the mill to the masterbatch and the stock sheeted out for curing. For the radiation study, the filler-rubber masterbatch was divided into two portions. One aliquot was sheeted out and submitted for radiation. To the second portion, the conventional sulfur curing ingredients were added on a mill and the mixture sheeted out for curing. All sheets were 0.075 in. gage.

The peroxide and sulfur vulcanized compounds were cured between aluminum foil in preheated laboratory presses at 2000 psi and 153° C and 142° C, respectively. Rubber-filler slabs were irradiated in air at the Stanford Research Institute under the direction of Dr. Richard Glass, using a 1-Mev resonant transformer at the rate of 7×10^6 reps/min. Half of the total radiation dose was applied to each side of the slab.

Physical testing of vulcanizates was carried out by customary procedures. Crosslink density, η, was determined by equilibrium-swelling[9, 10].

For the peroxide study, the compounds were cured with dicumyl peroxide (90% purity, Hercules), 1.8 PHR, and contained either no filler or 50 PHR of filler as noted. In the radiation work, the compounds were formulated as follows (Table I). The respective sulfur cured controls were compounded as shown in Table II.

DISCUSSION OF RESULTS

Peroxide cure.—In Figure 1, the development of crosslinks as a function of time of cure is shown. The curves indicate that the optimum cure time for all compounds is similar, and that the contribution of filler to crosslink density over that of the unfilled control, is substantial for all fillers. The extent of the contribution of the filler is more apparent by a consideration of the value of the crosslink ratio η/η_0 (Table III). The crosslink ratios listed in Table III reveal that the filler contribution of the silica filled peroxide cured compound, where the decomposition mode of the curing agent is unaffected (Hi-Sil 101), approaches that of HAF black. Kraus[5] in his work found only a 20% "black contribution" ($\eta/\eta_0 = 1.2$) for an HAF black filled dicumyl peroxide-cured

TABLE II

FORMULATIONS FOR SULFUR CURE

	A-S	B-S	C-S	D-S	E-S	F-S
No. 1-RSS	100	100	100	100	100	100
Antioxidant[a]	—	2	—	—	2	—
Hi-Sil 233	—	—	29.3	58.5	58.5	—
Philblack 0	—	—	—	—	—	54.0
Curatives[b]	16	16	16	16	16	16

[a] Antioxidant 2246 (American Cyanamid), 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol).
[b] Antioxidant 2246, 1.0; 2,2′-dithiobisbenzothiazole, 0.8; di-o-tolylguanidine, 1.2; triethanolamine, 2.0; sulfur, 3.0; stearic acid, 3.0; zinc oxide, 5.0.

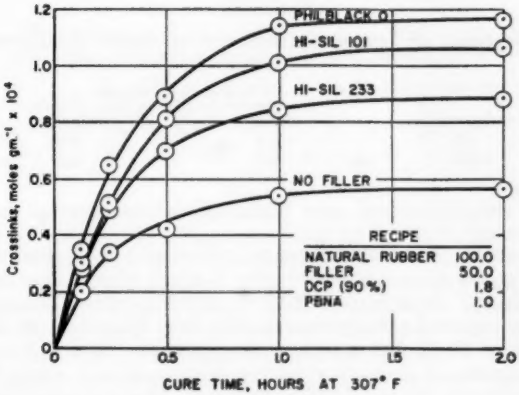

FIG. 1.—Effect of fillers on crosslinking in dicumyl peroxide (DCP)-cured natural rubber.

SBR compound. In a neutral or alkaline environment, dicumyl peroxide thermally decomposes in a homolytic manner to free radical fragments which initiate the crosslinking process during cure[7]. Acid catalyzed decomposition, however, yields ionic intermediates which do not promote crosslinking[11]. Apparently the more neutral Hi-Sil 233 contains a few acid sites on its surface. In the vicinity of these sites, the peroxide decomposes ineffectually.

A simple calculation shows that the amount of peroxide used should yield 0.6×10^{-4} moles of crosslinks/g rubber—assuming one crosslink per mole of peroxide. On this basis, the efficiencies of crosslinking for the unfilled, the Hi-Sil 233-filled and the Hi-Sil 101-filled compounds are 100%, 160% and 190%, respectively.

Radiation cure.—The production of crosslinks in the radiation cure is a linear function of dosage, whether the elastomer is unfilled or filled with fine particle silica or carbon black (Figure 2). Arnold and his coworkers[12] reported a similar result for compounds containing HAF black in SBR or Hevea irradiated by spent-fuel elements. As measured by the value of the η/η_0 ratio, the filler contribution to crosslink density increases with loading of silica as would be desirable in a fully reinforcing filler (Table IV). Such behavior is common with highly reinforcing blacks in conventional curing systems. As usual, however, the η/η_0 value for sulfur cured compounds filled with the silica did not change with loading. The filler contribution by Hi-Sil 233 in the radiation cured compounds is large as compared to that found in the usual

TABLE III

CROSSLINKS AND FILLER (50 PHR) CONTRIBUTIONS AT OPTIMUM CURE[a] DICUMYL PEROXIDE IN HEVEA

Filler	pH	Crosslinks $\times 10^4$, moles/g	η/η_0
None	—	0.56	—
Hi-Sil 233	7.0	0.88	1.6
Hi-Sil 101	9.0	1.06	1.9
Philblack 0	8.8	1.16	2.1

[a] 120 min at 153° C.

TABLE IV

COMPARISON OF FILLER CONTRIBUTION OF HI-SIL 233 LOADED COMPOUNDS, SULFUR OR RADIATION CURED

Loading volume	η/η_0 at Optimum cure	
	Sulfur[a]	Radiation[b]
15	1.1	2.0
30	1.1	3.6

[a] 30 min. at 142° C.
[b] 8×10^7 reps.

sulfur vulcanizates. For radiation cures, the filler contribution to reinforcement (η/η_0) in the silica compound also is much higher than in the black mixture (Table V). As reflected by 100% modulus values, Lamm and Madelaine[13] recently reported a similar observation from their work on the radiation of Philblack 0 or Hi-Sil 233 natural rubber mixtures by a Co^{60} source in air. Thus, the potential of silica to reinforce elastomers in a compatible curing system, equivalent to the most efficient blacks, appears unequivocal.

Because of possible oxidation effects which might be encountered during radiation in air 2 PHR of a sterically hindered phenol [2,2′-methylene-bis(4-methyl-6-*tert*-butylphenol)] was added, respectively, to a sample of unfilled rubber (compound B-R) and to one containing 30 volumes of silica (compound E-R). The results are summarized in Table VI.

The silica increases the efficiency of the crosslinking reaction initiated by radiation by a factor of about 4 whether the antirad is present or not. The magnitude of constancy of the efficiency factor F, for this antirad was surprising considering the limited resonance structures for the molecule. The G values for crosslinking found here for irradiation of the unfilled sample in air are in excess of those generally reported in the literature[13].

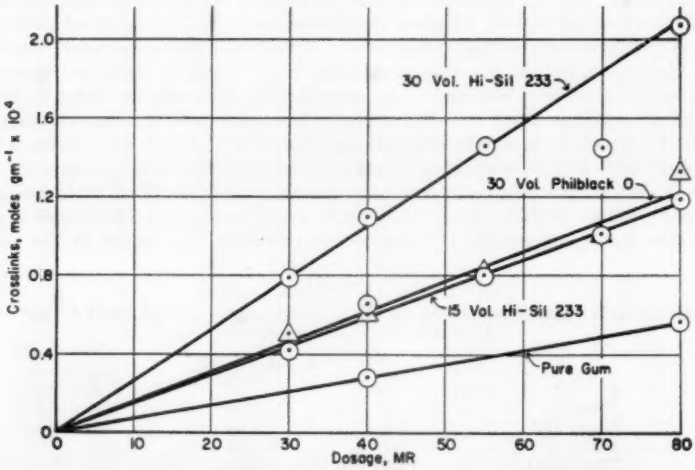

FIG. 2.—Effect of fillers on crosslinking in radiation-cured natural rubber.

TABLE V

COMPARISON OF FILLER CONTRIBUTION OF RADIATION CURED SILICA AND HAF BLACK LOADED COMPOUNDS (30 VOLUME LOADING)

Filler	η/η_0 at Optimum cure[a]
Hi-Sil 233	3.6
Philblack 0	2.3

[a] 8×10^7 reps.

The silica vulcanizates for this study were prepared chiefly for structural studies and no attempt was made to obtain an optimum balance of physical properties. In general, however, properties such as tensile were lower inthe radiation than in the sulfur cures. These differences are shown in Table VII and compared with similar results reported by other investigators[12, 14, 15]. Noting that the tensiles of peroxide and radiation cures were lower than those of similarly filled sulfur vulcanized compounds, Pinner[15(e)] blamed the relatively rigid carbon-carbon linkages between polymer chains. He advanced the concept that the sulfide bonds present in sulfur cures are more easily broken when stressed thus permitting chain redistribution and alignment before reforming and, finally, the crystallization necessary for high stress.

TABLE VI

EFFECT OF FREE RADICAL SCAVENGER[a] ON CROSSLINKING IN RADIATION CURE[b]

Filler	G, η/100 ev: Without additive	G, η/100 ev: With additive	F[c]
None	0.74	0.35	0.50
Hi-Sil 233, 30 vols.	2.7	1.4	0.48

[a] 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol), 2 PHR.
[b] Dose: 8×10^7 reps.
[c] Fraction of crosslinks stopped, $F = \left[1 - \frac{\eta \text{ (with additive)}}{\eta \text{ (without additive)}}\right]$.

SUMMARY

The potential of fine particle silica to reinforce elastomers to an extent comparable with the most efficient furnace blacks has been indicated by the extent and nature of bound rubber formation. This potential has been confirmed in peroxide and radiation cures by the increase in crosslink density of the filled over the unfilled natural rubber mixtures. Confirmation in these curing systems stimulates further research designed to realize this high potential not fully attained in present sulfur cures.

TABLE VII

COMPARISON OF TENSILE STRENGTH IN RADIATION AND SULFUR CURES

Filler	Loading, PHR	Tensile at optimum cure, psi: Radiation	Tensile at optimum cure, psi: Sulfur	Reference
Hi-Sil 233	58	2830[a]	3890[b]	This work
Hi-Sil 233	60	4050	3510	Reference 12
Philblack 0	45	1950	4150	Reference 14
Furnace black	40	2230	4560	Reference 15(a)
None	—	1900	3700	Reference 15(d)

[a] cure: 8×10^7 reps.
[b] cure: 30 min at 142° C.

ACKNOWLEDGEMENT

The assistance of Mr. Gerald Humes in this investigation is gratefully acknowleged.

REFERENCES

[1] Studebaker, M. L., RUBBER CHEM. & TECHNOL. **30**, 1400 (1957).
[2] Bachmann, J. H., Sellers, J. W., Wagner, M. P. and Wolf, R. F., RUBBER CHEM. & TECHNOL. **32**, 1286 (1959).
[3] Wagner, M. P. and Sellers, J. W., *Ind. Eng. Chem.* **51**, 961 (1959).
[4] Laning, S. H., Wagner, M. P. and Sellers, J. W., *J. Appl. Polymer Sci.* **2**, 225 (1959).
[5] Kraus, G., *Rubber World* **135**, 67, 254 (1956); RUBBER CHEM. & TECHNOL. **30**, 928 (1957).
[6] Bueche, A. M., *J. Polymer Sci.* **15**, 105 (1955); RUBBER CHEM. & TECHNOL. **28**, 865 (1955).
[7] Dannenberg, E. M., Jordan, M. E. and Cole, H. M., *J. Polymer Sci.* **31**, 127 (1958); cf. also Parks, C. R. and Lorenz, O. Presented at the Meeting of the Division of Rubber Chemistry of the American Chemical Society, Buffalo, N. Y., May, 1960.
[8] Charlesby, A., "Atomic Radiation and Polymers," Pergamon Press, New York, 1960.
[9] Flory, P. J. and Rehner, John, Jr., *J. Chem. Phys.* **11**, 512 (1943).
[10] Adams, H. E. and Johnson, B. L., *Ind. Eng. Chem.* **45**, 1539 (1953); RUBBER CHEM. & TECHNOL. **26**, 741 (1953).
[11] Kharasch, M. S., Fono, A. and Nudenberg, W., *J. Org. Chem.* **15**, 748 (1950).
[12] Arnold, P. M., Kraus, Gerard and Anderson, H. R., Jr., *Kautschuk u. Gummi* **12**, WT 27 (1959); *Rubber and Plastics Age* **40**, 836 (1959); Kraus, G., U. S. 2,964,457 (1960).
[13] Bauman, R. J., *J. Appl. Polymer Sci.* **2**, 328 (1959); Turner, D. T., *J. Polymer Sci.* **27**, 503 (1958); RUBBER CHEM. & TECHNOL. **31**, 737 (1958).
[14] Lamm, G., Lamm, A. and Madelaine, H., *Kautschuk u. Gummi* **13**, WT 80 (1960).
[15] (a) Dogadkin, B. A., Tarasova, Z. N., Kaplunov, M., Karpov, V. and Klauzen, N., *Kolloid., Zhur.* **20**, 260(1958); RUBBER CHEM. & TECHNOL. **32**, 785(1959); (b) Nikitina, T. S., Kuzminskil, A. S., Oksentevich, L. A. and Karpov, V. L., "Proceedings of the First All-Union Conference on Radiation Chemistry," p. 275 (1957); (c) Johnson, B. L., Adams, H. E. and Barzan, M., *Rubber World* **137**, 73 (1957); (d) Gehman, S. D., and Auerbach, I., *Intern. J. Appl. Radiation and Isotopes* **1**, 102 (1956); (e) Pinner, S. H., *ibid.*, **5**, 121 (1959).

RADIATION CROSSLINKING OF RUBBER. YIELDS OF HYDROGEN AND CROSSLINKS*

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INTRODUCTION

On exposure to high energy radiation natural rubber is crosslinked[1, 2] and hydrogen[2] evolved. Similar and more extensive observations on polyethylene have been interpreted as indicating that one molecule of hydrogen is evolved for each crosslink formed[3]. As free radicals have been detected by paramagnetic resonance studies[4], and their presence has been inferred from reactions with monomers and oxygen, considerable support has been given to the simple crosslinking mechanism outlined by the following reactions[3], in which RH represents polyethylene:

$$\mathrm{RH} \longrightarrow \mathrm{R}\cdot + \mathrm{H}\cdot$$
$$\mathrm{H}\cdot + \mathrm{RH} \longrightarrow \mathrm{R}\cdot + \mathrm{H}_2$$
$$2\mathrm{R}\cdot \longrightarrow \mathrm{R{-}R}$$

The yield of crosslinks has been estimated from stress-strain and swelling measurements by reference to simple rubber elasticity theory. Properly, for use in stoichiometry, an estimate should be derived of the yield of carbon-carbon crosslinks. This requires corrections to be made for the influence of the initial molecular weight of the polymer, radiation-induced fracture, and entanglements. Such corrections require a detailed knowledge which is only available for natural rubber and which has been applied in the present paper.

Evidence for free radical intermediates in the radiation crosslinking of polyethylene is not conclusive and an alternative ionic mechanism has been proposed[5]. In the present paper the possibility of free radical precursors of crosslinks and hydrogen has been investigated by use of scavengers.

EXPERIMENTAL MATERIALS AND METHODS

The unpurified rubber was a commercial sample of pale crêpe containing 30 per cent gel and 2.3 per cent of acetone-soluble nonrubber constituents. Similar samples of pale crêpe were masticated in air to give soluble rubbers of varying molecular weights. These were continuously extracted with acetone at about 50° C in the dark and under nitrogen for 24 hours and then dried and stored *in vacuo* (*A* and *B*). Rubber *C* was a similarly treated deproteinized rubber supplied by the United States Rubber Company. Osmotic molecular weights and elemental analyses were kindly undertaken under the supervision, respectively, of Miss M. A. Place and Dr. W. T. Chambers.

* Reprinted from *Polymer* 1, pages 27–42 (1960).

	Osmotic molecular weight M	Oxygen (%)	Nitrogen (%)
Rubber A	2.22×10^5	0.6	0.3
Rubber B	3.13×10^5	0.5	0.3
Rubber C	$c.\ 5 \times 10^5$	0.15	0.03

Chemicals were of analytical or laboratory reagent grade and 1,1-diphenyl-2-picryl hydrazyl (D.P.P.H.) was kindly supplied by Dr. W. F. Watson. The polyisoprene squalene

$$CH_3 \cdot C(CH_3) : CH \cdot CH_2 \cdot [CH_2 \cdot C(CH_3) : CH \cdot CH_2]_4 \cdot CH_2 \cdot CH : C(CH_3) \cdot CH_3$$

was purified by a method recommended by Dr. P. W. Allen[6] from a commercial sample and had a carbon-hydrogen ratio corresponding closely to the above formula.

Preparation of samples.—The weighed rubber was packed into glass break-seal tubes (diameter 0.8 cm: wall thickness 0.1 cm) and silica tubes (diameter 0.4 cm: wall thickness 0.5 mm). Solids were added to benzene solutions of rubber which were then 'freeze dried', and liquids were added directly with a micrometer syringe. The rubber and any liquids were thoroughly degassed and the tubes sealed at $<10^{-4}$ mm Hg pressure.

Irradiation of samples.—At Wantage Radiation Laboratory the tubes were exposed to the electron beam from a 4 MeV linear accelerator. Throughout the exposure the tubes were cooled with a blast of cold air and the temperature of the rubber, as measured occasionally with an injection pyrometer immediately after irradiation, was never more than 50° C. Tubes immersed in a stream of liquid nitrogen were usually cracked or shattered by explosions when irradiated. This was avoided by using the silica tubes which were located during irradiation in a close-fitting, thin-walled polyethylene tube through which flowed liquid nitrogen. Comparative samples were obtained under similar conditions but with either water or air cooling. These experiments were undertaken with the co-operation of Mr. J. McCann and Mr. F. Hazell of the Technological Irradiation Group.

Dosimetry measurements were made by Mr. J. McCann with a water calorimeter and checked at low doses[7] by simultaneous exposure of reaction tubes containing cyclohexane[8] ($G(H_2) = 5.3$). In other cases the derived value for rubber of $G(H_2) = 0.64$ was used.

A few samples were irradiated in a Co^{60} source with an ambient temperature of about 30° C under the supervision of Mr. P. Ridout (T.I.G.).

Measurement of gaseous products.—The samples were examined two or more days after irradiation. The gaseous products, volatile in various temperature ranges, were compressed into a known volume with a Töpler pump and the pressure observed on a silicone oil manometer. A technique of this kind has been described by Moore and Watson[9].

Estimation of crosslinks.—Equilibrium swelling values were determined at 25° C in *n*-decane as described by Moore and Watson. Values were obtained only for samples containing more than 90 per cent gel and no correction was made for the relatively small number of crosslinks in the sol fraction. Values for the elastic network parameter C_1 were obtained from the swelling data by the use of calibration curves which had been determined by Mullins[10] for rubber networks prepared *via* thermal decomposition of di-*tert*-butyl peroxide. C_1^∞ was calculated from Mullins's empirical relationship (1)

$$C_1^\infty = C_1 + 6.2 M_0^{-1} \times 10^{10} \text{ dyn} \qquad (1)$$

and the moles of physical crosslinks per gram of rubber calculated from the expression

$$C_1^{\infty} = \tfrac{1}{2}RTM_e^{-1}(\text{phys.})$$

as $\frac{1}{2}M_e^{-1}(\text{phys.}) = 4.39 \times 10^{-11}C_1^{\infty}$.

Corresponding estimates of chemical crosslinks, $\frac{1}{2}C_c^{-1}(\text{chem.})$, were obtained from calibration curves of $M_c^{-1}(\text{phys.})$ with $M_c^{-1}(\text{chem.})$ which had also been formulated from data for the peroxide system[11].

In order to take account of chain fracture the correction (1) must be applied not with the initial molecular weight of the rubber, M_0, but instead with the actual value for the crosslinked molecules in the network, M. This can be derived from Equation (2) in which β is the ratio of fractures to chemical crosslinks.

$$M = M_0(1 + \tfrac{1}{2}M_c^{-1}(\text{chem.})M_0\beta)^{-1} \qquad (2)$$

An average value[12] for β of 0.14 was used with the above uncorrected value of $\frac{1}{2}M_c^{-1}(\text{chem.})$ to calculate an approximate value of M. This was used in equation (1) to calculate a further value of $\frac{1}{2}M_c^{-1}(\text{phys.})$ and thence $\frac{1}{2}M_c^{-1}(\text{chem.})$. The latter value was used again in Equation (2) and the process repeated to give successively closer approximations to the true values which do take account of fracture.

The unsaturation of squalene.—This was estimated in carbon tetrachloride with iodine monochloride (reaction time 1 hour) and also in benzene with perbenzoic acid (reaction time 4½ hours)[13].

EXPERIMENTAL RESULTS AND DISCUSSION

Gaseous yields.—Almost all the gas which had separated from purified rubber at room temperature was volatile in the range −196 to −183° C and mass spectrometric analysis (kindly undertaken by Professor J. C. Robb of Birmingham University) showed it to comprise mostly hydrogen (Tables 1 and 2). The accurately linear relationship between the yield of gas volatile in the range −196 to −183° C, subsequently referred to simply as hydrogen, and the radiation dose is shown in Figure 1. The calculated value of $G(H_2)$ for rubber is 0.64.

The formation of hydrogen together with a small amount of methane is the expected consequence of bond fracture in a polyisoprene. Additionally,

TABLE I

GASEOUS FRACTIONS FROM IRRADIATED RUBBER

Rubber	Nominal dose at 0.7 Mrad/min	Temperature range of fraction	$10^3 \times$ yield of gas (mole/g rubber)
Rubber *C*		− 196 to − 183° C	3.50
	50 Mrad	− 78° C	0.04
		about 15° C	0
Same sample after 40 h at 70° C		− 196 to − 183° C	0.02
	—	− 78° C	0.04
		about 15° C	0.55
Unpurified rubber		− 196 to − 183° C	3.39
	50 Mrad	− 78° C	0.27
		about 15° C	0.02
Same sample after 40 h at 70° C		− 196 to − 183° C	0.03
	—	− 78° C	0.04
		about 15° C	0.55

TABLE 2

ANALYSIS OF GASEOUS YIELD IN MASS SPECTROMETER

Nominal dose (Mrad)	Gas at N.T.P. (cm^3)	Hydrogen (%)	Methane (%)
150	1.8	99	1
200	2.1	99.7	0.3

Before irradiation the degassed rubber *C* was heated 50 h at 100° C *in vacuo*.

as there are about three random fractures of the main chain of carbon atoms per twenty crosslinks, there is also the likelihood that hydrocarbon fragments are present in the rubber. As these may not have escaped from the bulk of rubber the tubes were heated for 40 hours at 70° C *in vacuo*. Under these conditions a volatile fraction was detected and also a very small amount of an involatile oily liquid was observed to separate from the rubber. No quantitative significance could be attached to these results because a similar, although smaller, effect was observed with unirradiated controls from which the volatile fraction formed by heating *in vacuo* was never satisfactorily removed.

The gaseous products formed by the radiolysis of rubber apparently differ significantly from those resulting from its photolysis. In the latter case Bateman[14] has reported that only about 80 per cent of the gas volatile at room temperature is hydrogen and that the remainder comprises low molecular weight hydrocarbons. A similar difference in gaseous products has already been mentioned by Weiss[15] for polyethylenes.

As mentioned previously, Charlesby had a sample of the gas formed by exposure of unpurified rubber to radiation from an atomic pile examined in a mass spectrometer and found that it consisted almost entirely of hydrogen with only a small amount of methane and higher molecular weight products. Consistent results were obtained in the present experiments except that an appreciable fraction distilled at −78° C (Table 1). This fraction is presumably due largely to nonrubber constituents and is detected with careful outgassing.

Estimated yields of crosslinks.—The broken line in Figure 2 shows estimated yields of physical crosslinks when a correction is made only for the initial molecular weight of the rubber. The upper limit of the crosslinking range

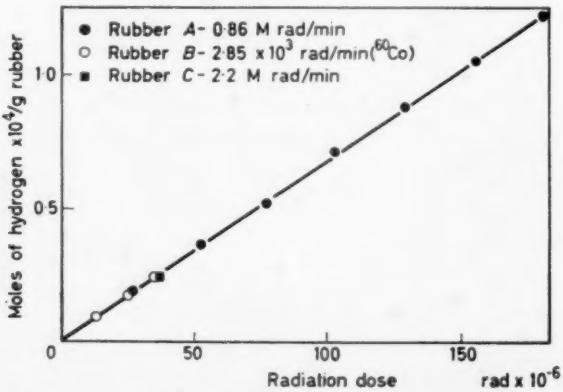


FIG. 1.—Yield of hydrogen.

corresponds to the region beyond which extension stress-strain measurements cannot satisfactorily be made and, therefore, for which no calibration with swelling measurements has been provided. The range may be extended by use of the Flory-Huggins equation but if a μ value is chosen to fit the middle values[10] then, as noted in other work[9], divergingly higher estimates are obtained for higher degrees of crosslinking. Charlesby used a Flory-Huggins equation in his work on radiation crosslinking and concluded that the degree of crosslinking was proportional to the dose over an enormous range of values provided

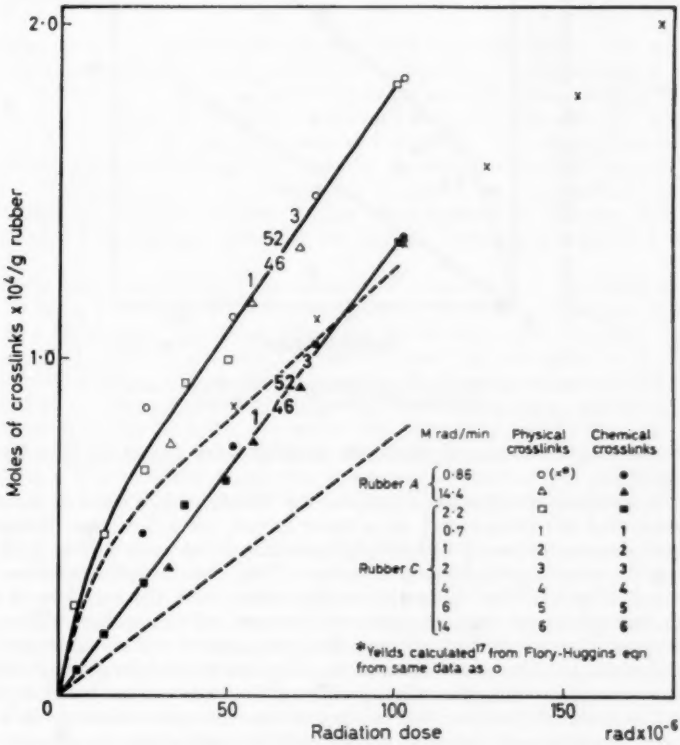


FIG. 2.—Estimated yields of crosslinks. (β = 0.14). Broken lines give estimates of crosslinks when no correction is applied for chain fracture.

the rubber was assumed to include some crosslinks prior to exposure. In fact, even with a completely soluble rubber a curve of the characteristic shape shown in Figure 2 is observed when physical crosslinks are plotted against some linear measure of chemical crosslinking such as the radiation dose, and Flory[16] has pointed out that this is probably due to a contribution to the elasticity from entanglements. This view has been developed quantitatively by Mullins[10] and by Moore and Watson[9] and their work allows a separation of physical crosslinks into chemical, in this case carbon-carbon, crosslinks and entanglements.

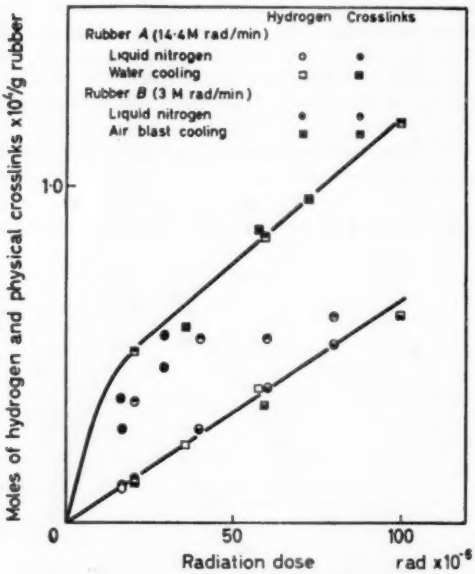


FIG. 3.—Yields of hydrogen and physical crosslinks on irradiation at low temperatures. (No β correction.)

Corresponding estimates of chemical crosslinks are shown by the straight broken line.

The estimate of chemical crosslinks by Moore and Watson is based on evidence that *tert*-butoxy and, to a lesser extent, methyl radicals formed by thermal decomposition of di-*tert*-butyl peroxide react with rubber solely by abstracting α-methylenic hydrogen atoms. They then adduced evidence from related studies with low molecular weight olefins that the sole fate of these allylic radicals would be to combine and so crosslink the rubber. Therefore, the number of moles of chemical crosslinks per gram of rubber was determined by analysis as $\frac{1}{2}$ (moles of *tert*-butanol plus methane formed per gram of rubber). Further data concerning the validity of the above estimate are currently being sought in these laboratories, but in view of the reasonable relationship found[9] between physical and chemical estimates it is satisfactory to proceed with studies of the present kind in the expectation that, *in toto*, only minor revision will be required later.

A method has already been described above by which an allowance can be made for chain fracture when estimating the yield of crosslinks. The value of 0.14 for β was obtained as the average of the values 0.11 and 0.18 which were calculated previously from experimental data[12] and which are believed to bracket the true value. This value for β was used in Equation (2) to estimate the actual molecular weight of the crosslinked molecules and thence to take into account the influence on the swelling data of network chains terminated by only one crosslink. It should be noticed that the empirical correction used (Equation 1) was determined by Mullins for up to about two fractures per

TABLE 3

ESTIMATED YIELDS OF CROSSLINKS ON EXPOSURE TO Co^{60} γ-RADIATION

		Rubber *A*		Rubber *B*		
Dose (Mrad)		28.3	39.4	14.5	26.2	36.6
No β correction	$\frac{1}{2}M_c^{-1}$(phys.)	0.75	0.93	0.40	0.59	0.75
	$\frac{1}{2}M_c^{-1}$(chem.)	0.40	0.56	0.14	0.27	0.40
Corrected for $\beta = 0.14$	$\frac{1}{2}M_c^{-1}$(phys.)	0.97	1.23	0.47	0.74	0.77
	$\frac{1}{2}M_c^{-1}$(chem.)	0.60	0.83	0.18	0.40	0.61
G[X(chem.)]		2.0	2.0	1.2	1.5	1.6

molecule, caused by shearing the rubber prior to crosslinking. The present data are concerned with up to about five fractures per molecule but there is some justification for the extrapolation in so far as Mullins's correction[10] corresponds to a fraction of elastically ineffective network chains of 2.5 $M_cM_0^{-1}$ which is close to Flory's proposed value of 2 $M_cM_0^{-1}$. The effect of correcting for fracture is to raise G[X(chem.)] from the previously reported[17] value of 0.75 to 1.3. These are in good agreement with corresponding values of 0.8 and 1.05 determined by a different method[12]. The lower estimate of 1.05 may partly be attributed, in the present terms, to its implicit inclusion of a lower β value of 0.11.

Within experimental error the amount of crosslinking on exposure to the electron beam is independent of the dose rate in the range investigated of from 0.7 to 14 Mrad/min. However, assuming the same β value, a rather higher G[X(chem.)] value of average 1.6 was obtained on γ-irradiation at about 3×10^{-3} Mrad/min. Only a limited number of estimates were made and these confined to the less reliable lower degree of crosslinking range on account of the impracticability of using the source for exceedingly long exposures (see Table 3). If the higher value is significant it may be indicative of a dose rate dependence and so differ from results generally reported for polyethylene. However, further experimental work would be required to establish this possibility.

Yields of hydrogen and crosslinks at low temperatures.—On irradiation in liquid nitrogen the rubber darkened but rapidly regained its former transparency on warming. This may be due to trapped radicals which persist in highly viscous polymers for a considerable time even at room temperature[4, 18].

The results shown in Figure 3 indicate that the yield of hydrogen is not affected significantly by lowering the temperature of irradiation to approximately $-196°$ C while the swelling data show that either the yield of crosslinks is markedly reduced or, alternatively, that there is considerably more chain fracture. Variations in the swelling results may be due to lack of careful control of the warming up period.

Black[19] has reported appreciably lower G(X) values for polyethylene when irradiated at low temperatures, and similar observations have been made by Charlesby and Davison[20] who additionally observed that the yield of hydrogen remained constant. Contrary to these findings Lawton, Balwit and Powell[3] have reported a decreased yield of hydrogen at low temperatures and a similar trend in crosslinking provided the polymer was subsequently warmed to allow radicals trapped in the crystalline regions to react.

Effect of additives on yields of hydrogen and crosslinks.—It is known that crosslink formation in rubber exposed to radiation from an atomic pile is markedly reduced by scavengers which intercept hydrocarbon radicals[21].

TABLE 4

EFFECT OF ADDITIVES ON YIELDS OF HYDROGEN AND PHYSICAL CROSSLINKS (NO β CORRECTION)

Additive	$10^4 \times$ Product (mole/g rubber)		Fractional decrease in yield	
	H_2	X	H_2	X
1. 10^{-4} mole/g rubber				
Hydroquinone	4.20	9.75	−0.09	0.17
Diphenylamine	4.03	7.07	−0.05	0.40
No additive	3.98	12.2	—	—
Benzoquinone	3.91	8.75	—	0.25
No additive	3.72	11.15	—	—
D.P.P.H.	3.66	5.90	0.05	0.50
m-Dinitrobenzene	3.57	5.71	0.07	0.51
Diphenyl disulphide	3.33	4.90	0.14	0.58
Hexachloroethane	2.96	19.7	0.23	−0.69
2. 3×10^{-4} mole/g rubber				
tert-Butyl mercaptan	3.85	7.05	−0.12	0.09
No additive	3.44	7.75	—	—

Nominal doses: series 1: 55 Mrad, series 2: 51 Mrad.

Such radicals would be formed as a result of homolytic fracture of carbon-hydrogen bonds (i) and by reactions (ii) and (iii), in which RH represents rubber hydrocarbon.

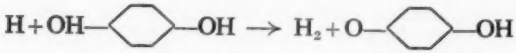
$$\mathrm{RH} \rightarrow \mathrm{R}\cdot + \mathrm{H}\cdot \qquad \text{(i)}$$

$$\mathrm{H}\cdot + \mathrm{RH} \rightarrow \mathrm{R}\cdot + \mathrm{H_2} \qquad \text{(ii) abstraction}$$

$$\mathrm{H}\cdot + \mathrm{RH} \rightarrow \mathrm{RH_2} \qquad \text{(iii) addition}$$

Data consistent with these reactions are shown in Table 4 concerning the effect of various scavengers on the yield of hydrogen. Reduced yields may be attributed to a reaction such as (iv) and increased yields, with additives containing carbon-hydrogen bonds of low energy, to one such as (v).

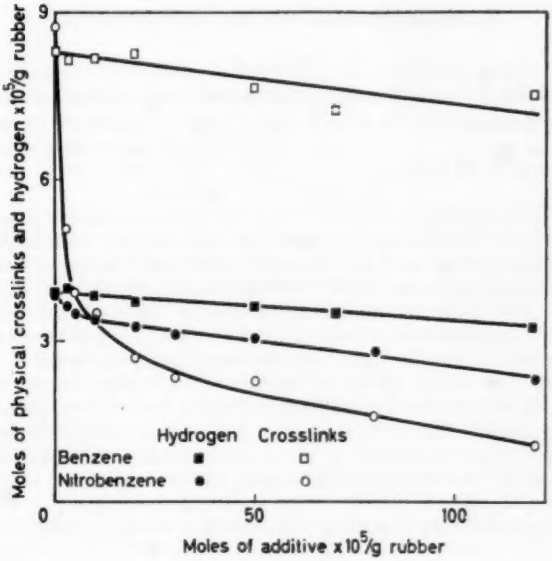
$$\mathrm{H}\cdot + \mathrm{CCl_4} \rightarrow \mathrm{HCl} + \cdot\mathrm{CCl_3} \qquad \text{(iv)}$$



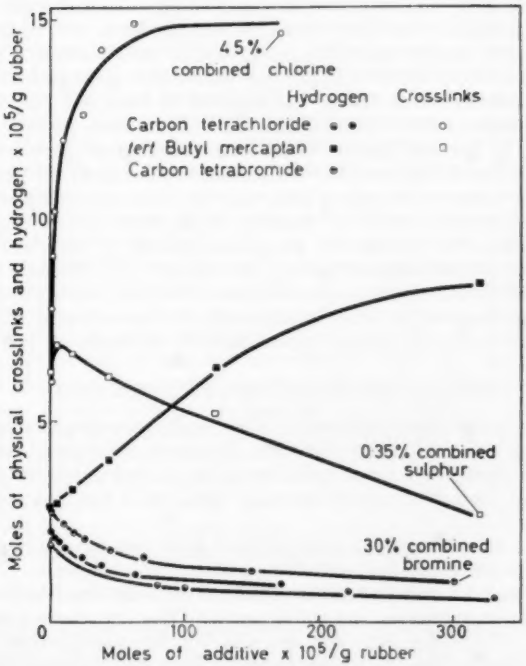
(v)

However it should be noticed that because the isoprene unit is itself very reactive towards hydrogen atoms significant changes in the yield of hydrogen can only be detected when much larger concentrations of scavenger are present than would normally be tolerated in studies of this kind. In these circumstances there may also be energy transfer effects which might either decrease the yield of hydrogen through protection of the rubber or else increase the yield by sensitized decomposition of an additive containing weak carbon-hydrogen bonds. This latter possibility may be important in accounting for the large yields of hydrogen formed in the presence of *tert*-butyl mercaptan (Figure 4b).

Figure 4(a) illustrates the two most general effects of additives on the yields of hydrogen and crosslinks. Benzene, chosen as an example of an additive which does not react readily with allylic radicals, reduces the yield of hydrogen with a parallel reduction in the yield of crosslinks. Its effect may stem either from the scavenging of hydrogen atoms or by excitation transfer from the rubber to benzene, which is the explanation favored by Manion and Burton[22] in accounting for the related effect of the reduced yield of hydrogen from cyclohexene when irradiated in the presence of benzene. In either case, the result



(a)



(b)

FIG. 4.—Effect of additives on yields of hydrogen and physical crosslinks (no β correction). Rubber C was used—each series a simultaneous exposure—with a dose rate of about 0.9 Mrad/min.

TABLE 5

CHANGES IN THE UNSATURATION OF SQUALENE ON IRRADIATION

Dose (Mrad)	0	40	80	128	170	213	242
Unsaturation (%)	95	91.2	91.0	88.9	87.4	87.1	85.4
C = C reacted $\times 10^4$ (mole/g)		5.8	5.9	8.9	11.3	11.7	14.2

may be taken as qualitatively indicative of the low crosslinking potential of the hydrogen atom. Nitrobenzene, which does react readily with allylic radicals, produces the expected marked decrease in the yield of crosslinks. At low concentrations nitrobenzene, like 1,5-dinitronaphthalene[21], is so efficient that apparently more than one crosslink is stopped for each molecule present. However, a more quantitative treatment of this efficiency in terms of chemical crosslinks must be deferred until data are available on the possible influence of additives on the extent of chain fracture. At higher concentrations the efficiency is much too low to be accounted for in terms of competition with a crosslinking reaction due to combination of randomly formed allylic radicals.

Figure 4(b) illustrates some of the complications which may obscure conclusions based on the effect of additives on yields of hydrogen and crosslinks. It is, perhaps, significant that the three additives shown are of the type which undergo radical addition reactions, sometimes involving chains, with double bonds[22].

Changes in the unsaturation of squalene on irradiation.—Davidson and Geib[24] described their early attempts to follow any change of unsaturation of rubber, with iodine monochloride, after very short exposures to pile radiation as not very illuminating but as indicating a decrease in unsaturation. According to more extensive recent work[25] unsaturated elastomers undergo marked changes and, in particular, natural rubber was reported to have lost 50 per cent of its initial unsaturation after a dose of 240 Mr. As no such marked change had been evident in infrared studies[26] further chemical data were sought. It is considered that such data cannot be satisfactorily obtained with networks and therefore experiments were undertaken with the hexaisoprene squalene. Little change in unsaturation could be detected using iodine monochloride but the figures obtained were considered unreliable because of substitution. More reliable estimates were obtained with perbenzoic acid and these show that there is a definite but relatively small consumption of double bonds (Table 5). The marked change reported by other workers may be due to failure of the reagent, iodine monobromide, to diffuse quantitatively throughout the crosslinked networks.

MECHANISM OF HYDROGEN FORMATION

It has been pointed out previously that a possible reaction in which hydrogen is formed from adjacent carbon atoms in the same molecule of rubber hydrocarbon would most likely occur with formation of conjugated triene unsaturation and it has been shown experimentally that such a reaction is of negligible importance[26].

The effect of additives on the yield of hydrogen provides evidence for hydrogen atom precursors but only for a part of the total yield. Thus, Figure 4(b) shows that both carbon tetrabromide and carbon tetrachloride reduce the yield markedly at relatively low concentrations but then have a much diminished effect. While the data are not suitable for quantitative analysis by competition kinetics, they do indicate qualitatively that a part of the hydrogen is scavenged relatively easily. The fraction of the hydrogen which escapes the scavenger is much more clearly defined in saturated hydrocarbons. For ex-

ample, according to Dewhurst[27], in the radiolysis of *n*-hexane 30 per cent of the hydrogen stems from a reaction yielding double bonds, 40 per cent can be repressed by scavengers of hydrogen atoms, and the remaining 30 per cent is ascribed to the 'molecular' reaction (vi).

$$2C_6H_{14} \longrightarrow H_2 + C_{12}H_{26} \qquad \text{(vi)}$$

A reaction analogous to (vi) in rubber would result in the formation of one molecule of hydrogen per chemical crosslink and its occurrence would help to explain two difficulties which appear if reference is made simply to reactions (i)–(iii). Firstly, it would help to account for the small or negligible change in the yield of hydrogen at very low temperatures (Figure 3) which otherwise could only be explained by supposing that the activation energies for the abstraction and addition reactions are equal. This seems to be unlikely, although the question has not been definitely resolved (see, for example, Ref. 28). Secondly, on the basis of reactions (i)–(iii) followed by crosslink formation by radical combination, the experimental ratio of about two chemical crosslinks per molecule of hydrogen requires that reactions (ii) and (iii) should occur to equal extents. Generally, however, the view is held that addition of hydrogen atoms to double bonds is much more frequent than abstraction of α-methylenic hydrogen atoms. For example, Melville and Robb[29] assume that this is the fate of all hydrogen atoms removed by collision with a range of olefins. However, further data would be desirable on this point since Darwent and Roberts[28] have reported that in the case of propylene the ratio of addition to abstraction is 4 to 5, and the latter reaction would be more favored in the isoprene unit which contains four more α-methylenic carbon-hydrogen bonds of lower energy. A further point which could be explained by reference to a 'molecular' reaction would be the failure of large concentrations of scavenger to stop all the crosslinks, but in this case a radical combination reaction is involved and so an alternative explanation would be provided by the formation of dense clusters of radicals in spurs.

The 'molecular' reactions of radiation chemistry are variously ascribed to the formation of radical clusters in spurs, to ions, and to 'hot' radicals. In the case of polyethylenes the reactions of both ions and 'hot' radicals have been invoked to account for crosslink formation in a partly crystalline medium in which the diffusion of polymer radicals would be severely restricted. The diffusion control of crosslink formation in rubber, which is a highly viscous liquid, would be far less critical but, nevertheless, there are the above experimental facts which are most satisfactorily explained by reference to a 'molecular' reaction. More explicitly, as suggested by Pravednikov, Yin-Shen-Kan and Medvedev[30] for polyethylenes, the absorption of high energy radiation by rubber would result in the formation of both 'thermal' and 'hot' hydrogen atoms. The 'thermal' hydrogen atoms would probably add preferentially to double bonds and the 'molecular' reaction would be a consequence of the preferential reaction of 'hot' atoms, after a relatively limited number of collisions, with the more abundant carbon-hydrogen bonds.

MECHANISM OF CROSSLINKING

Irradiation of rubber hydrocarbon results in the formation of mostly allylic and some alkyl radicals. Following Moore and Watson[9], these radicals, designated R·, are believed to combine to form crosslinks by reaction (vii).

$$2R\cdot \longrightarrow R{-}R \qquad \text{(vii)}$$

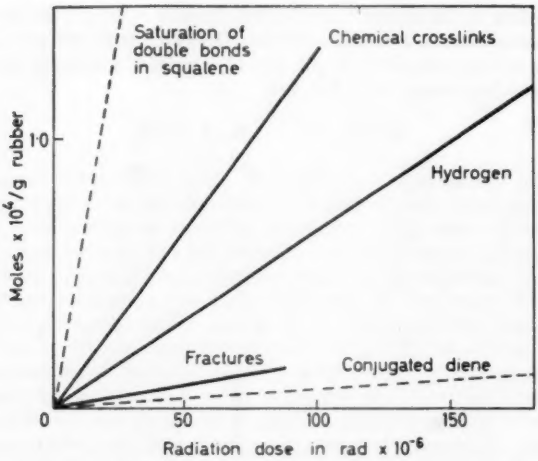


FIG. 5.—Yields of products on irradiation of polyisoprenes. The broken lines are only approximate representations.

If two allylic radicals disproportionate a conjugated diene group would be formed but such a reaction has already been shown to be of only secondary importance[26], as may also be judged from Figure 5. A further reaction which appears possible is crosslink formation by radical addition to double bonds, as indicated in reaction (viii), but such a reaction has been rejected by Moore and Watson on the grounds that corresponding reaction products are not formed in radical reactions in related low molecular weight olefins.

$$R\cdot + RH \longrightarrow R_2H\cdot \qquad \text{(viii)}$$

Presumably, addition crosslinking would only assume importance under conditions where isolated radicals are formed and where an alternative fate to combination with a second radical is favored. This possibility might account for the higher degree of crosslinking at lower dose rates (Table 3) and also for the observation by Roberts and Mandelkern[31] that, on irradiation, crystalline rubber crosslinks more readily than amorphous rubber.

A further possibility is that crosslinks may be formed as a result of chain fracture. Such a reaction is also judged to be of no more than secondary importance by reference to Figure 5 and, in particular, to the results of stress-relaxation studies which presumably would detect fracture even if followed by recombination into the network with formation of trifunctional crosslinks[32].

The results obtained following irradiation at low temperatures (Figure 3) are not explicable simply by reference to reactions (i)–(iii) and (vii) and are the subject of further investigation.

ACKNOWLEDGMENTS

Irradiation facilities were provided by the Technological Irradiation Group at Wantage Radiation Laboratory and Dr. R. Roberts and his colleagues are thanked for their much valued co-operation. Mr. G. T. Jones is thanked for

his help with the experimental work and Dr. E. G. Cockbain for suggestions on the presentation of the paper. This work forms part of the research program of The Natural Rubber Producers' Research Association.

SYNOPSIS

Purified natural rubber was irradiated *in vacuo* with a 4 MeV electron beam at dose rates of the order 10^6–10^7 rad/min. The gas evolved comprised almost entirely hydrogen. The yield of carbon-carbon crosslinks was estimated from swelling data with corrections for the influence of the initial molecular weight of the rubber, chain fracture, and entanglements, as $G(X) = 1.3$. When irradiated at $-196°$ C the rubber assumed an intense color which rapidly disappeared when it was allowed to warm up. Under these conditions $G(H_2)$ was little changed but the yield of crosslinks was apparently markedly reduced. The value of $G(H_2)$ was not affected by irradiation at room temperature at relatively low dose rates (10^3 rad/min:Co^{60}) but there was a limited amount of data indicating a higher $G(X)$ value of about 1.6. The yield of hydrogen could be markedly reduced with large amounts of an additive such as carbon tetrachloride. However, increased yields were obtained with additives which contained a weak carbon-hydrogen bond, e.g. hydroquinone. These effects have been discussed in terms of competition by the additive for hydrogen atoms which otherwise undergo metathetical and addition reactions with isoprene units. The reduction of unsaturation on irradiation of a hexaisoprene, squalene, was found to be very much smaller than previously reported estimates for the polyisoprene rubber.

REFERENCES

[1] Newton, E. D., U.S. Patent 1,906,402 (1929).
[2] Charlesby, A., *Atomics* **5**, 12 (1954).
[3] Lawton, E. J., Balwit, J. S. and Powell, R. S., *J. Polym. Sci.* **32**, 257 (1959).
[4] Schneider, E. E., *Disc. Faraday Soc.* **19**, 158 (1955).
[5] Collyns, B. G., Fowler, J. F. and Weiss, J., *Chem. & Ind. (Rev.)* **74**, (1957).
[6] Allen, P. W., To be published.
[7] Guenter, W. S., Hardwick, T. J. and Nejak, R. P., *J. Chem. Phys.* **30**, 601 (1959).
[8] Schuler, R. H. and Allen, A. O., *J. Amer. Chem. Soc.* **77**, 5 (1955).
[9] Moore, C. G. and Watson, W. F., *J. Polym. Sci.* **19**, 237 (1956).
[10] Mullins, L., *J. Polym. Sci.* **19**, 225 (1956).
[11] Mullins, L., *J. Appl. Polym. Sci.* To be published.
[12] Mullins, L. and Turner, D. T., *J. Polym. Sci.* To be published.
[13] Kolthoff, I. M., Lee, T. S. and Mairs, M. A., *J. Polym. Sci.* **2**, 199 (1947).
[14] Bateman, L., *J. Polym. Sci.* **2**, 1 (1947).
[15] Weiss, J., *J. Polym. Sci.* **29**, 425 (1958).
[16] Flory, P. J., Rabjohn, N. and Schaffer, M. C., *J. Polym. Sci.* **4**, 225 (1949).
[17] Turner, D. T., *J. Polym. Sci.* (Part II), **35**, 541 (1959).
[18] Chapiro, A., *J. Chim. phys.* **53**, 295 (1956).
[19] Black, R. M., *Nature, Lond.* **178**, 305 (1956).
[20] Charlesby, A. and Davison, W. H. T., *Chem. & Ind. (Rev.)* 232 (1957).
[21] Manion, J. P. and Burton, M., *J. Phys. Chem.* **56**, 560 (1952).
[22] Cf. Kharasch, M. S., Jensen, E. V. and Urry, W. H., *J. Amer. Chem. Soc.* **69**, 1100 (1947).
[23] Davidson, W. L. and Geib, I. G., *J. Appl. Phys.* **19**, 427 (1948).
[24] Kuzminskii, A. S., Nikitina, T. S., Zhuravskaya, E. V., Oxentievich, L. A., Sunitsa, L. L. and Vitushkin, N. I., *2nd United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva.* Preprint A/Conf. 15/P/2085 (1958).
[25] Evans, M. B., Higgins, G. M. C. and Turner, D. T., *J. Appl. Polym. Sci.* To be published.
[26] Dewhurst, H. A., *J. Phys. Chem.* **62**, 15 (1958).
[27] Cf. Darwent, B. de B. and Roberts, R., *Disc. Faraday Soc.* **14**, 55 (1953).
[28] Melville, H. W. and Robb, J. C., *Disc. Faraday Soc.* **14**, 55 (1953).
[29] Pravednikov, A. N., Yin-Shen-Kan and Medvedev, S. S., *2nd United Nations International Conference on the Peaceful Uses of Atomic Energy.* Preprint A/Conf. 15/P2294 (1958).
[30] Roberts, D. E. and Mandelkern, L., *J. Amer. Chem. Soc.* **80**, 1289 (1958).
[31] Charlesby, A., *Proc. Roy. Soc. A*, **231**, 521 (1955).

MECHANOCHEMICAL REACTIONS LEADING TO REINFORCEMENT. II. NATURAL RUBBER AND PHENOLIC RESINS *

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INTRODUCTION

The reaction of polyfunctional metallic salts and, in particular, aluminum alkoxides, with natural and synthetic rubbers when subjected to mechanical scission has been reported previously[1]. The gelation of natural rubber by mechanicochemical reactions can be achieved by a variety of chemical reagents. However, this communication will be restricted to phenolic resins and their intermediates, the phenol alcohols.

Electron micrographs of unvulcanized natural rubber containing 72 to 80 per cent of gel, prepared by masticating acetone extracted rubber with various phenolic resins under nitrogen for periods of 30 minutes, show no indication of particles of resin or resin rich zones. The complete dispersion of the resins at concentrations of 1 to 2 per cent on a molecular scale indicates that the gelation centers must be molecular, as in the case of aluminum isopropoxide and not particulate as with carbon black gel. Chemical reaction of the active chains produced by mechanical scission of the rubber must therefore take place with reactive groups attached to the resin molecules. By analogy with the previous work in this field it would be expected that each resin molecule must have an average number of reactive functional groups in excess of two if it is to be capable of entering into gelation reactions. To test this hypothesis and to obtain data on the reactivity of different functional groups, a series of mastications of natural rubber with phenols and phenol alcohols with functionalities of 1, 2, 3, 4 and 6 were carried out.

Phenolic resins have an established utility as reinforcing agents for natural and synthetic rubbers. Reinforcement by the presence of gel in the absence of reinforcing particles has been shown in the case of aluminum isopropoxide for peroxide cured vulcanizates. Similar stress-strain investigations have therefore been carried out with resin gelled natural rubber.

EXPERIMENTAL METHODS AND PROCEDURES

Gelling agents.—The following eight commercially available phenol-formaldehyde resins of varying types were ground in a vibro mill, so as to pass through a 120 mesh, prior to use.

Cellobond H 831, a phenol-formaldehyde resin (British Resin Products, Ltd., Sully, Penarth).

Elo C 460, a cresol-formaldehyde resin (Birkbys, Ltd., Liversedge, Yorkshire).

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 36, pages 211–224 (1960). This paper was presented at the Journées Francaises des Plastiques et due Caoutchouc, Paris, in May, 1960.

Synphorm P 25/C, a phenol-formaldehyde resin (Blackburn & Oliver, Ltd., Pemberton, Wigan).
CM 57, a phenol-formaldehyde novolac resin (Watts, Ltd., London).
R 17321, a heat reactive phenolic resin (Bakelite, Ltd., Birmingham).
CM 295, a xylenol-formaldehyde resin (Watts, Ltd., London).
AR 39, an ortho-cresol-formaldehyde resin (C. Lowe & Co. (Manchester), Ltd., Stockport).
Bedesol 99, a phenol-formaldehyde resin (Imperial Chemical Industries, Ltd., Gloucester House, London).

The resin intermediates used as model compounds with known functionality were prepared according to established syntheses except for phenol, benzyl alcohol, resorcinol, catechol, hydroquinone, saligenin, *p*-hydroxy-benzyl alcohol, Bis-phenol A, pyrogallol, hydroxy-quinol, phloroglucinol, trimethylol propane, tetramethylol methane, and hexahydroxy-cyclo-hexane which were commercial compounds of B.P. grade. In general the phenol alcohols 2,4-dimethylol-phenol, 2,6-dimethylol 3-cresol, 2,4,6-trimethylolphenol, 3,3′,5,5′-tetramethylol-4,4′-dihydroxy-diphenyl methane and 2,3,5,6-tetramethylol hydroquinone were prepared by the reaction of the appropriate phenol with formaldehyde under conditions giving high yields of the required compounds[2–7].

Rubber.—Thin sheets of pale crepe with an initial Wallace plasticity of 63 (Mooney number 27) and having a nitrogen content of 0.1 per cent and an oxygen content of 0.7 per cent were used without homogenization by milling

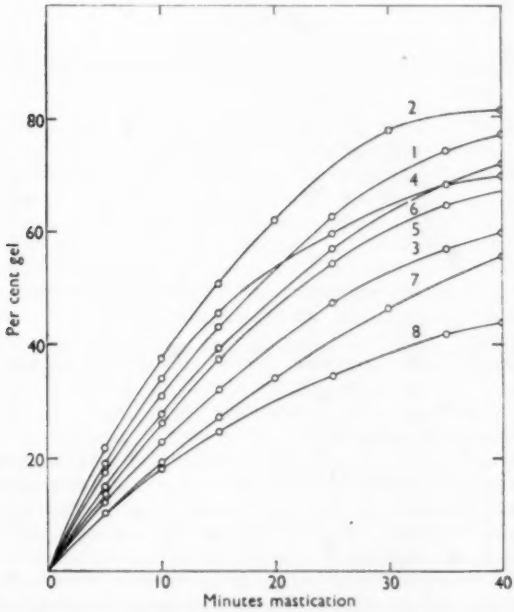


FIG. 1.—1% of each resin masticated with acetone extracted rubber under nitrogen. *1.* Cellobond H831 *2.* Elo C460. *3.* Synphorm P25/C. *4.* CM 57. *5.* R 17321. *6.* CM 295. *7.* AR 39. *8.* Bedesol 99.

so as to retain the high molecular weight (limiting viscosity number in benzene (η) = 5.7). Chemical analysis, solution viscosity, and Wallace plasticity measurements on samples from different portions of the same batch of pale crepe showed variations within the limits of experimental error only. For the experiments with "extracted rubber" the pale crepe was Soxhlet-extracted with acetone for 24 hours and stored under vacuum until required for use.

The rubber used in these experiments was from the same batch as used in Part I for studying the reactions with aluminum isopropoxide and related compounds.

Methods.—The gelation experiments were carried out in a Baker Perkins Uni-Rotor Masticator[8] fitted with the spiral type of scrolls which were rotated

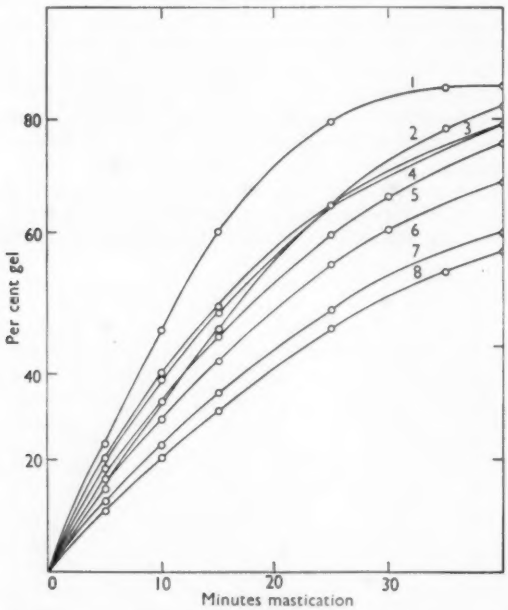


FIG. 2.—1% of each resin masticated with acetone extracted rubber under nitrogen. *1.* Cellobond H831 *2.* Elo C460. *3.* Synphorm P25/C. *4.* CM 57. *5.* R 17321. *6.* CM 295. *7.* AR 39. *8.* Bedesol 99.

at 100 rpm. Additional experiments were carried out on a David Bridge 12 × 6 inch two-speed mixing mill.

The percentage gel in the masticated sample and the degree of swelling of the gel fractions were determined by allowing 0.1 g of the rubber, contained in a glass thimble with a coarse sintered base, to reach equilibrium whilst immersed in 10 ml of Analar benzene. The thimble, rubber, and benzene were contained in 2 × 1 inch glass weighing bottles which were maintained at room temperature in the dark for 6 days before measurements were carried out. Gel contents were obtained by determining the concentration of 2.5-ml aliquots of the centrifuged sol fraction. The gel swelling indexes (grams of benzene per gram of rubber gel) were calculated from the weight *in situ* after removing non-

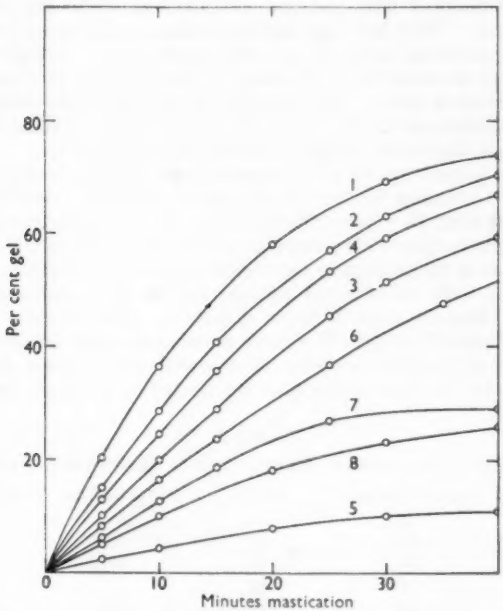


FIG. 3.—1% of each resin masticated with acetone extracted rubber under nitrogen. *1.* Cellobond H831. *2.* Elo C460. *3.* Synphorm P25/C. *4.* CM 57. *5.* R 17321. *6.* CM 295. *7.* AR 39. *8.* Bedesol 99.

absorbed benzene from the gel surface and from the glass thimble with filter paper. Corrections for the sol fraction in the gels were made.

Ten gram portions of the rubber together with the appropriate weight of additive were masticated for 5 seconds before flushing out the masticator with nitrogen. This procedure was adopted to minimize the loss of finely-powdered additives during the flushing out process. After the appropriate period of mastication with a chamber volume of 10.5 ml, the rubber was removed from the chamber and approximately 0.2 g of the rubber was retained for gel content measurement. The bulk of the rubber was then returned to the masticator and mastication continued for further periods of time, 0.2-g samples being removed between mastications. The mastication chamber was cooled by immersing in a water bath which was maintained at 12 ± 1° C by the addition of small quantities of ice.

Since the experiments with the small masticator indicated a fast reaction under conditions of maximum shear, sheets of pale crepe were dusted with the powdered resins or intermediates and passed through the tightest nip obtainable with full water cooling on the two rolls (12° C) for the milling experiments.

Results. Variation of Gel Content with Extent of Mastication.—The rates of gelation of acetone extracted rubber masticated with 1 per cent of each of the phenolic resins in an atmosphere of nitrogen were all of the same order, Figure 1. Mastications carried out for less than 5 minutes gave low gel contents (less than 10 per cent) and the gels were highly swollen and easily dispersed. Extrapolations of the gel content figures obtained for mastications of 5 minutes and

longer were consistent with gelation commencing with the application of mechanical shear. With the most reactive resin a maximum gel content of 83 per cent was achieved after 40 minutes mastication. Longer mastication times, within the order of 60 to 150 minutes, were required to obtain maximum gelation for the other resins. Gel contents at the maximum varied from 73 to 85 per cent. Continued mastication resulted in a slight decrease in gel content but this was not significant during mastications up to 3 hours.

An increase in the concentration of resin present during mastication resulted in a small but consistent increase in the rate of gelation. Acetone extraction of the products after 20 minutes mastication showed increasing quantities of acetone extractable resin with increasing initial resin contents, Table 1.

Gel formation in the presence of free radical acceptors.—In general mastication under nitrogen with unextracted natural rubber gave somewhat lower gel contents with the same series of resins (Figure 2). Gel contents were reduced still further (Figure 3), if the resins were masticated with extracted rubber in the presence of atmospheric oxygen. The lowest gel contents were obtained when unextracted natural rubber was masticated in air with the same series

TABLE 1

GEL CONTENT AND ACETONE EXTRACT AFTER MASTICATION WITH CM57

Resin, %	Minutes mastication	Gel, %	Gel swelling	Acetone extract, %
0.5	5	—	—	nil
	10	15	—	nil
	20	44	35	nil
1.0	5	18	—	0.28
	10	34	32	0.05
	20	56	28	nil
2.0	5	28	—	0.96
	10	47	32	0.35
	20	71	27	0.06
5.0	5	41	25	3.72
	10	67	21	3.56
	20	89	18	3.34

of resins, Figure 4. In the presence of 0.5 per cent of thio-2-naphthol gelation was inhibited except for the two most reactive resins which gave a lower overall gel content which reached a maximum after 40 minutes mastication, Figure 5. The order of reactivity of the resins remained more or less the same under different mastication conditions.

Effect of shear rate on the gelation of rubber with resins.—The rate of shear was reduced by (*a*) changing the design of the masticating scrolls; (*b*) raising the temperature of the temperature control bath; (*c*) reducing the rotor speed; and (*d*) plasticization of the rubber with solvent, Figure 6. Except when examining the effect of shear rate, mastications were carried out under conditions of maximum obtainable shear rate, i.e. mastication at 12° C with spiral scrolls rotating at 100 rpm.

Gel formation on a two roll mill.—Six thin sheets of unextracted pale crepe were plied up with 1 per cent of resin dusted between sheets. Increasing gel contents were obtained when the plied sheets were subjected to up to 20 passes through a 0.005 inch nip of the two roll mill with roll temperatures of 15° C, running at friction speeds. After 20 passes the gel content for Resin 1 decreased, whilst that for Resin 2 continued to increase but to a lower maximum

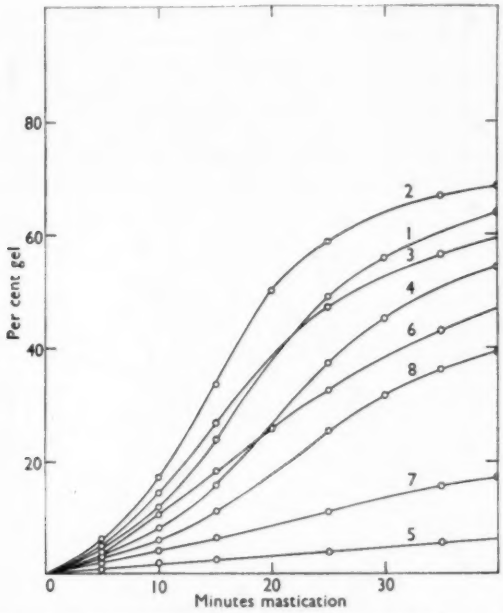


FIG. 4.—1% of each resin masticated with acetone extracted rubber under nitrogen. *1.* Cellobond H831. *2.* Elo C460. *3.* Synphorm P25/C. *4.* CM 57. *5.* R 17321. *6.* CM 295. *7.* AR 39. *8.* Bedesol 99.

gel content of approximately 8 per cent. Negligible gel contents were recorded for the other resins, Figure 7.

Stress-strain measurements on pregelled vulcanizates.—Gum stocks gelled with 1 per cent of each of the two most reactive resins were prepared by mastication under nitrogen in the Uni-Rotor Masticator and by mastication

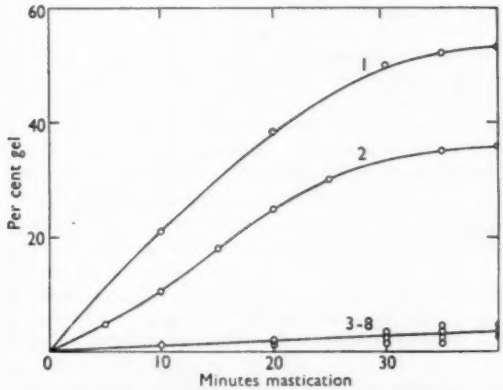


FIG. 5.—Acetone extracted natural rubber masticated with 1% of each of the Resins 1 to 8 (cf Fig. 1) in the presence of 0.5% of thio-2-naphthol.

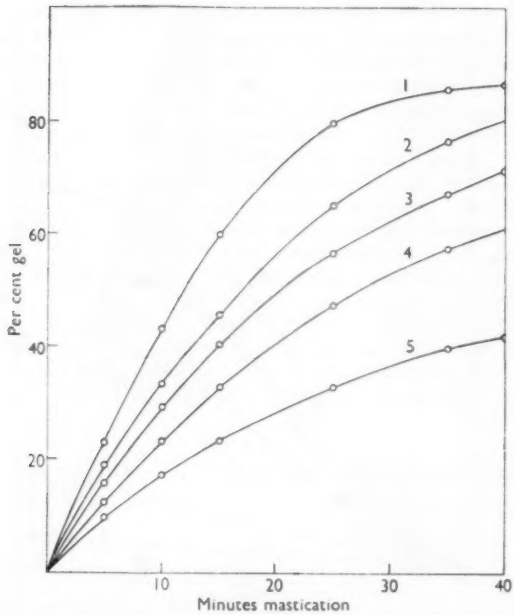


FIG. 6.—Natural rubber masticated under nitrogen wth 1% of the resin Cellobond H831 with varying conditions of shear. *1.* Spiral scrolls, 100 rpm, 12° C. *2.* Plow scrolls, 100 rpm, 12° C. *3.* Plow scrolls, 100 rpm, 50° C. *4.* Plow scrolls, 80 rpm, 50° C. *5.* Spiral scrolls, 100 rpm, 12° C, plasticized with 30 pph of benzene.

to 20 passes on the two roll mill. Each stock was compounded with dicumyl peroxide on a warm mill (90° C) to facilitate dispersion and minimize degradation of the gel network. Control stocks were given similar mastication, milling and compounding ingredients. The tensile data for these two systems are compared with the controls in Figures 8 and 9.

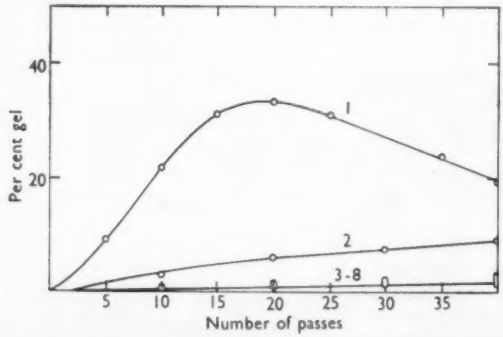
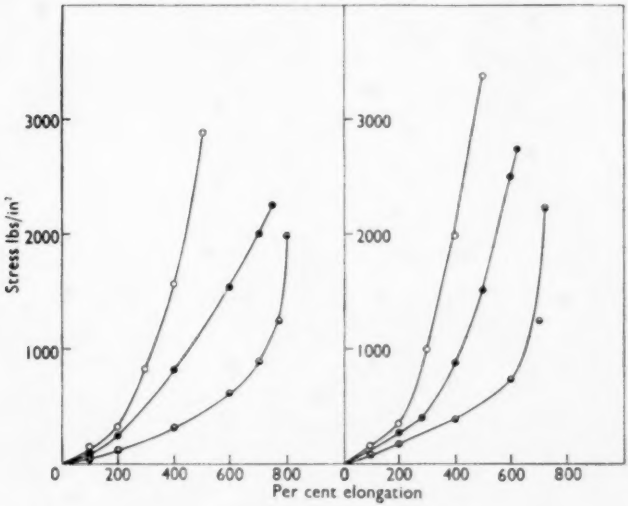


FIG. 7.—1% of each resin masticated with acetone extracted rubber under nitrogen. *1.* Cellobond H831. 2. Elo C460. *3.* Synphorm P25/C. *4.* CM 57. *5.* R 17321. *6.* CM 295. *7.* AR 39. *8.* Bedesol 99.

Gelation with model compounds.—The concentration of model compounds to be used as the gelation agents was calculated on the basis of 6×10^{-4} mole per 10 g of rubber. This was equivalent to 1 mole per 250 isoprene units approximately. The functionality, gel content, gel swelling, Wallace plasticity of the masticated rubber and limiting viscosity number of the benzene soluble fraction for each of the 20 model compounds is recorded in Table 2. Gel content, swelling, plasticity and solution viscosity in each case were measured after 20 minutes mastication in the laboratory masticator under nitrogen.



FIGS. 8 AND 9.—○ 1% of Cellobond H831. ● 1% of Elo C460. ◒ Control. Vulcanization: 3% of dicumyl peroxide, 50 mins at 140° C.

DISCUSSION

The concentration of phenolic resin required to achieve greater than 75 per cent of gel after 40 minutes mastication is of the order of 1 per cent compared with 20 per cent for carbon black and 0.005 per cent for aluminum isopropoxide[1]. The carbon black gel formation has been shown to be a mechanicochemical reaction between the carbon black particles and the sheared rubber chains (polymeric free radicals)[9]. The small concentration of gelation reagent required in the case of the alkoxides and similar compounds is indicative of a chemical reaction between the molecules of additive and the reactive chain ends. In an attempt to differentiate between a particulate and a chemical interaction, electron micrographs of rubbers containing greater than 75 per cent of gel prepared by mastication of extracted rubber with 2 per cent of Resin CM57, Cellobond H831 and R17321, respectively, were recorded. The resins appeared to be completely compatible and no resin particles were observed. It was therefore considered that interaction with resins was chemical rather than particulate in its mechanism.

The phenol-formaldehyde resins used as gelling agents contained differing average numbers of phenolic and residual methylol groups according to the

TABLE 2

GEL CONTENT AND CHARACTERISTICS FOR RESIN INTERMEDIATES AND MODEL COMPOUNDS

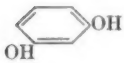
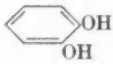
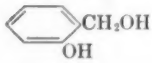
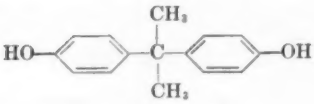
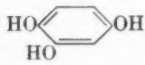
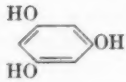
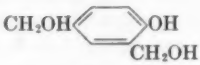
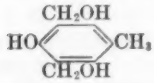
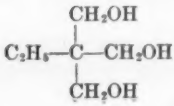
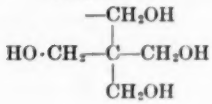
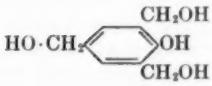
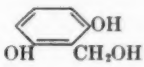
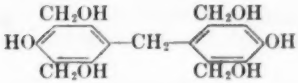
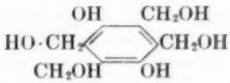
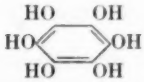
	Compound	Functionality	Percent gel	Gel swelling	Wallace plasticity	Limiting viscosity number $[\eta]$ (g^{-1} ml^3)
	None	–	nil	—	65	498
1.		1	nil	—	62	405
2.		1	nil	—	65	416
3.		2	nil	—	56	485
4.		2	nil	—	55	445
5.		2	nil	—	57	436
6.		2	nil	—	59	456
7.		2	nil	—	61	463
8.		2	nil	—	59	428
9.		3	17	*c.* 40	87	510
10.		3	19	*c.* 38	83	495
11.		3	27	*c.* 35	91	487
12.		3	35	32	90	517
13.		3	41	34	89	516
14.		3	47	28	95	537

TABLE 2 (*Continued*)

	Compound	Functionality	Percent gel	Gel swelling	Wallace plasticity	Limiting viscosity number [η] (g^{-1} ml^{3})
15.		4	55	29	97	614
16.		4	67	23	99	645
17.		3	78	20	100	504
18.		6	89	16	100	318
19.		6	94	17	100	174
20.		6	95	16	100	189

manner of preparation and manufacture. These differences could be advanced as an explanation for variations in rate and extent of gelation, Figure 1. The effects of radical acceptor, Figures 2 to 4, were as expected for a mechanicochemical reaction. The presence of radical acceptors, i.e., nonrubber constituents, added radical acceptors or atmospheric oxygen, provided a competitive reaction which consumed the reactive free radicals preventing either recombination or reaction with reactive groups that were present in the resin. The failure of thio-2-naphthol to completely suppress the gelation reaction for the two most reactive resins was an anomaly which could not be explained on the exclusive basis of a free radical mechanism Figure 5. Similar anomalous results were recorded in the case of aluminum isopropoxide[1].

The effect of shear rate, with the characteristic negative temperature coefficient, Figures 6 and 7, was indicative of a mechanicochemical reaction. The rate of shear determined the rate of gelation and therefore the rate of the reaction. Processes which increased the rate of shear (increases in rotor speed, changes in scroll design, etc.), increased the rate and extent of gelation.

If the gelation reaction proceeded by the interaction of ruptured rubber chains with reactive groups on the resin molecules then it should be possible to control the reactions by the number and type of functional groups in the resin. Since resins are complex mixtures of low molecular weight macromolecules this postulate was put to the test with model compounds containing phenolic and methylol groups. Typical phenol-formaldehyde resin intermediates were also included among the model compounds where such could be isolated.

In Table 2 it can be seen that a functionality of three is required before gelation occurs. This is in accordance with the formation of an insoluble three-dimensional network. When the rubber was masticated under nitrogen in the absence of additives there was little change in the Wallace Plasticity and only a small drop in the limiting viscosity number (from 570 to 498). With monofunctional reagents a lowering of both plasticity and solution viscosity was observed. Difunctional additives would be expected to act as linkages between the ruptured chains and this is consistent with both the Wallace Plasticities and the solution viscosities observed.

When the functionality is three or more gelation occurs and there is a consequent rise in the plasticity. The limiting numbers of the sol fractions rise at first and then fall off at about 75 per cent of gelation. This increase in solution viscosity can be explained by the chain lengthening of the multifunctional additives prior to gelation, and the fall off at high gel contents can be attributed to the incorporation of the majority of the larger rubber molecules into the gel network. The molecular weight of the residual sol rubber is less than that of the limiting chain length for mechanical scission. One hundred per cent gelation is not therefore to be expected from a mechanicochemical reaction.

The physical properties of the peroxide vulcanizates prepared from the gelled rubbers indicate a measure of reinforcement. No claim is made for having achieved the optimum curing conditions for the systems, or that conventional sulfur vulcanizates are similarly reinforced. A full evaluation is in progress[10]; initial results indicate that gelled rubbers, natural and synthetic, prepared in this way can be added to gum stocks to improve processing behavior during extrusion, calendering, etc.

Since the resins used in these experiments and the methylol derivatives employed as model compounds are known to form three dimensional networks on heating, benzene solutions of the "oil soluble" resins were refluxed with acetone extracted rubber under nitrogen. The solutions contained 3 per cent of rubber and 5 parts resin per 100 of rubber. No gelation occurred during 24 hours of refluxing but in most cases an insoluble residue was formed equal to or less than the weight of resin present.

The evidence presented whilst supporting an overall mechanochemical reaction does not allow an analysis of the individual steps of the mechanism to be made. Consideration of the retardation and inhibition reactions which occur during free radical vinyl polymerizations in the presence of phenolic, quinonoid and hydroquinonoid compounds suggests a number of possible reactions which could lead to peptization, chain coupling or gelation according to the functionality of the resin or model compound. Although less likely in the systems considered, the possibility of polar mechanisms must not be dismissed[1]. Further experimental work is in progress with a view to elucidating the reaction mechanisms and the nature of the crosslinks in the gelation networks.

SUMMARY

The reaction of polyfunctional metallic salts with natural rubber during mastication has been extended to gelation by phenolic resins. High gel contents are achieved by mastication with 1 to 2 per cent of resin in the absence of oxygen. By using polyphenols and phenol alcohols it has been shown that an average of at least three functional groups, —OH or —CH_2OH, per molecule

are required to achieve gelation. The presence of the gel network in the unvulcanized rubber gives an improvement in processing characteristics.

ACKNOWLEDGMENT

The author acknowledges the assistance of a Research Grant from Imperial Chemical Industries, Plastics Division, Welwyn Garden City, Herts., which has facilitated the work in this field. This project forms part of the research which is being undertaken at the National College of Rubber Technology.

REFERENCES

[1] Ceresa, R. J., *Trans. Inst. Rubber Ind.* **36**, 45 (1960).
[2] Freeman, J. H., *J. Am. chem. Soc.* **74**, 6257 (1952).
[3] Ullmann, F. and Brittner, K., *Ber.* **42**, 2539 (1909).
[4] Martin, R. W., *J. Am. Chem. Soc.* **73**, 3952 (1951).
[5] Seto S. and Horiuchi, H., *J. Chem. Soc. Japan, Ind. Chem. Soc.* **56**, 419 (1953).
[6] Seebach, F., *Ber.*, 1939, **728**, 1635; *Ber.* **73**, 1338 (1940).
[7] Carpenter, A. T. and Hunter, R. F., *J. Chem. Soc.* **1954**, 2731.
[8] Watson, W. F. and Wilson, D., *Rubber Age, Lond.* **38**, 982 (1957).
[9] Watson, W. F., *Proc. 3rd Rubber Technol. Conf., Lond.*, **1954**, 553.
[10] Ceresa, R. J., and Wynn, R., to be published.

GRAFT POLYMERS FROM PVC AND RUBBER *

A. A. Berlin, A. G. Kronman, D. M. Yanovskiĭ
and V. A. Kargin

Recently a large number of investigations into the production of graft and block polymers have been published. Considerable scientific and practical interest attaches to such polymers derived from synthetic and natural rubbers[1–4]. There have been no communications in the literature on the production of graft polymers of vinyl chloride with various rubbers. Moreover, in certain work[2] it is indicated that attempts to produce a graft block polymer of this nature by mechanochemical means, and also to graft vinyl chloride to rubber latexes, did not give satisfactory results.

We studied the possibility of producing graft copolymers of vinyl chloride with rubbers by a chain transfer reaction in the polymerization of vinyl chloride in coarse dispersions of rubber or in a solution of rubber in a monomer, and also under conditions of mastication of the polymers at high temperature. It was here supposed that the combination of PVC with small amounts of an elastomer having a low glass temperature was found to lower the brittle point temperature of the PVC and to raise its impact strength.

The selection, as one line of investigation, of the polymerization of vinyl chloride in coarse dispersions of rubber or in a solution of rubber in the monomer was determined by the fact that here (in contrast with grafting in latexes) we eliminate the presence of large amounts of emulsifier in the polymerization system, which of course reduces the yield of graft polymer. The grafting process was carried out both in the presence of emulsifiers (photo gelatin, sulfanol, polyvinyl alcohol) and without addition of emulsifying agents; in the former case a considerable portion of the rubber remained unreacted.

The rubber polymers (SKN-26 butadiene-nitrile, SKB butadiene, SKI isoprene, and natural rubbers), in the presence of which the polymerization of the vinyl chloride was effected, previously underwent careful freeing from antiagers and antioxidants by extraction with the appropriate solvents, and also reprecipitation, since the stabilizing additives act as inhibitors of radical polymerization. The polymerization of vinyl chloride in the presence of the rubbers was carried out in a 4-liter autoclave of special steel, fitted with a measurer and stirrer. Ammonium persulfate was used as the initiator.

The polymerization of vinyl chloride in the presence of rubber was carried out by two methods. The first consisted of prior swelling or dissolving of carefully purified rubber in the vinyl chloride at 40 to 70°, after which there is added to the autoclave a solution of initiator and the process of polymerization carried out.

In the second method there was added to the rubber, freed from the stabilizers, powdered ammonium persulfate, on the mill at room temperature, then the rubber along with water and the vinyl chloride was charged into the autoclave; the polymerization was carried out at 60 to 70°. Milling of the rubber

* Translated by R. J. Moseley from *Vysokomolekularnye Soedineniya* 2, 1188–92 (1960); a RAPRA translation.

TABLE 1

INFLUENCE OF THE TYPE OF RUBBER UPON THE MAIN STRENGTH CHARACTERISTICS OF THE COMPOSITIONS

Designation of rubber	Initial amount of rubber, in % of monomer	Impact strength, kgcm/sqcm*	Tensile strength, kg/sqcm	Relative elongation, %
PVC without rubber	—	8.6	550	82
SKN-26	5	6.8	489	12
SKB	5	4.2	476	8.4
Natural rubber	5	6.9	450	8.6
SKI	5	4.8	512	9.1

* The impact strength was determined on specimens of Viniplast of thickness 4 mm with a notch along the radius to a depth of 1 mm.

at low temperature was carried out with the aim of improving its solubility in vinyl chloride, which favors the process of grafting. It is well-known that in the process of cold milling there takes place a degradation of the polymer which is intensified on the addition of an initiator. Thus, for instance, in our experiments the relative viscosity of a 0.5% solution of natural rubber in cyclohexanone prior to milling was 1.5; after milling without initiator it was 1.461, while after milling with the addition of ammonium persulfate it was 1.175. After milling with ammonium persulfate the solubility of the rubber in vinyl chloride is significantly better. Thus in the polymerization of vinyl chloride in the presence of unmilled natural rubber and SKI, which only swell in the monomer, there is formed a nonuniform product, containing inclusions of unreacted rubber. When rubbers of these classes are used after milling with initiator there is formed a quite uniform product as a result of polymerization.

In the polymerization of vinyl chloride by the first and second methods in the presence of rubbers soluble in it (SKN-26 and SKB) there are formed uniform products of reaction. 'Viniplasts' produced on this basis have practically identical physicomechanical characteristics (specific impact strength, tensile strength, relative elongation).

Therefore in further work, with a view to establishing the most favorable conditions for grafting of vinyl chloride to rubbers, we carried out a prior cold mastication of the rubbers in the presence of ammonium persulfate.

The graft polymerization experiments were carried out with the amount of rubber in the original mixture 5% of the weight of the monomer. Before the addition of the vinyl chloride the autoclave was evacuated. On termination of the polymerization phenyl-2-naphthylamine is introduced into the autoclave.

For the production of Viniplast there were added to the products of reaction of vinyl chloride and rubber calcium stearate, litharge, phenyl-2-naphthylamine and transformer oil. The resulting compositions were milled for 10 to 15 minutes at 155 to 170°, and then subjected to molding for 25 to 40 minutes at a temperature 5 to 7° in excess of the milling temperature.

In Table 1 we show the mechanical properties of Viniplast produced on the basis of PVC modified by SKN-26, natural rubber, SKB and SKI. The glass temperature of the modified products is determined by the glass temperature of PVC (Figure 1).

None of the attempts to separate even one of the final reaction products by means of extraction with various solvents or with a mixture of the solvents gave positive results. The separation of the graft copolymer from the mixture produced in the interaction of vinyl chloride with rubbers and containing as

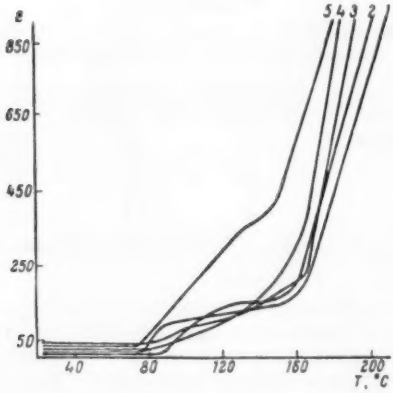


FIG. 1.—Dependence of deformation upon temperature for PVC-modified by rubbers. *1*—PVC; *2*—PVC + 5.5% of SKN-26; *3*—PVC + 5.5% SKB; *4*—PVC + 5.5% SKI; *5*—PVC + 5.5% natural rubber.

well as the reaction products the homopolymer PVC and unreacted rubber presents great difficulty in cases where the PVC and rubbers (natural rubber, SKB, SKI) have different solubility, not to speak of the separation of a mixture with components of like solubility (PVC and SKN-26). The position is further aggravated by the fact that as a result of the graft copolymerization effected by the chain transfer reaction there are formed along with the graft polymers PVC with a wide range of molecular weights, low-molecular destructurized rubber and also spatial structures.

The causes governing the formation of low-molecular PVC are the high temperature of the process (70°), the increased amount of initiator (1% of the monomer), and also the action of the rubber as a chain scission agent.

In view of the variety of products obtained in the above processes, the physicomechanical characteristics of Viniplast based on them fall short of the corresponding characteristics for a PVC Viniplast. It is well-known[5] that even for PVC by itself nonuniformity of molecular weight has an unfavorable influence upon the quality of Viniplast.

With polymerization of vinyl chloride in the presence of SKN-26 we obtain products (7 to 12%) which are insoluble in cyclohexanone at 80° over a period of 100 hours. The homopolymers (PVC and SKN-26) and also corresponding mixtures of components of analogous composition are highly soluble in cyclohexanone under considerably less severe conditions. The thermomechanical curve plotted for the insoluble portion of the product confirms the presence of three-dimensional structures (Figure 2). An analysis of the insoluble portion

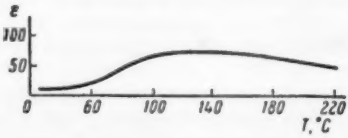


FIG. 2.—Dependence of deformation upon temperature for the insoluble fraction of the product obtained in the graft copolymerization of vinyl chloride and SKN-26.

of the product revealed the presence in it of 42.4% chlorine and 1.84% nitrogen.

The processing of rubber under conditions exactly reproducing the experiments with vinyl chloride in a solution of a substance not capable of polymerization (in our experiments we used in place of vinyl chloride its hydrogenation product, ethyl chloride) does not in general alter its solubility. Consequently, the presence of an insoluble product in the polymerization of vinyl chloride in the presence of rubbers is governed by the formation of a rubber network bound by chains of PVC. Analogous phenomena are observed in the grafting of styrene to natural rubber[6].

An attempt to prevent the formation of three-dimensional structures in the process of grafting, by the introduction of regulators (CCl_4, $CHCl_3$) did not meet with success. In the presence of a small addition of regulator (up to 1%) the reaction of graft polymerization did not take place and a mechanical mixture of the polymers was formed.

A possible mechanism of the action of the regulator in graft polymerization may be expressed by the following formulas[7]:

$$\mathrm{KaH} + \mathrm{R}\cdot \longrightarrow \mathrm{RH} + \mathrm{Ka}\cdot,$$

$$\mathrm{Ka}\cdot + \mathrm{CCl_4} \longrightarrow \mathrm{KaCl} + \mathrm{CCl_3}\cdot$$

$$\mathrm{CCl_3}\cdot + \mathrm{nM} \longrightarrow \mathrm{CCl_3} - (\mathrm{M})_n,$$

where KaH is the molecule of rubber, R the radical formed in the decomposition of the initiator, and M the molecule of monomer.

The ozonization of the resulting insoluble products of graft copolymerization of vinyl chloride with SKN-26 leads to a considerable improvement in their solubility on account of the scission of chains of rubber (under the conditions of the experiment PVC is stable to ozone).

A further line of investigation was the study of compositions based on PVC and various rubbers under conditions of mastication at high temperature. It was of interest to investigate the influence of the polarity of the rubbers upon the principal physicomechanical properties of Viniplast. With this purpose in view we prepared compositions on a basis of PVC (grade PF-4) and of natural, isoprene, butadiene, butadiene-styrene and chloroprene (Nairit) rubbers.

The results of physicomechanical testing of the resulting Viniplasts, prepared according to the above formula and technology, are collected in Table 2.

Judging from the properties of Viniplasts given in this Table, the rubbers containing polar groups (Nairit and SKN-26) raise the impact strength of the

TABLE 2

PHYSICOMECHANICAL PROPERTIES OF VINIPLAST WITH RUBBERS

Grade of rubber	Amount of rubber in composition, %	Impact strength with notch, kgcm/sqcm	Tensile strength, kg/sqcm	Relative elongation, %
PVC without rubber	—	8.6	550	82
Natural rubber	10	9.7	354	4.4
Butadiene rubber	10	6.7	350	5.8
Isoprene rubber	10	3.7	357	9.7
Nairit	10	16.5	437	81.5
Butadiene-nitrile rubber	10	34.6	551	100

Viniplast, while the nonpolar elastomers (SKB, SKI and natural rubber) are practically incompatible with PVC and lower the strength characteristics of articles based on it. On increasing the polarity of the rubber there is an improvement also in the strength characteristics of the resulting Viniplast. One indication of the incompatibility of PVC with natural rubber, SKI and SKB is the very low value of relative elongation, in spite of the fact of there being 10% of rubber in the composition.

The optimum physicomechanical properties belong to a Viniplast based on a PVC-SKN-26 composition. A significant improvement in the properties of the composition, in our opinion, is connected with the formation of hydrogen bonds between butadiene-nitrile rubber and PVC.

CONCLUSIONS

1. The authors investigate the graft copolymerization of vinyl chloride and butadiene-nitrile rubber by a chain transfer reaction, and also the combined mastication of PVC with various rubbers at elevated temperatures.

2. In physicomechanical properties Viniplasts produced on the basis of the products of graft copolymerization of vinyl chloride with butadiene-nitrile rubber, and also of the modification of PVC by butadiene, isoprene and natural rubbers are not superior to the corresponding characteristics of ordinary Viniplast.

3. In the combined mastication of PVC with Nairit and of PVC with butadiene-nitrile rubber at elevated temperatures compositions are produced which in respect of impact strength are 2 to 4 times superior to Viniplast from PVC.

4. It is suggested that the improvement in the physicomechanical properties in the combination of PVC with SKN-26 is connected with the formation of hydrogen bonds between the molecules of the polymers in question.

REFERENCES

[1] Bateman, L. C., *Ind. Eng. Chem.* **49**, 704 (1957).
[2] Bloomfield, G. F. and Swift, P. McL., *J. appl. Chem.*, No. 11, 609 (1955).
[3] Hart, R., *Ind. chim. belge* **21**, 1053 (1956).
[4] Allen, P. W. et al., *Rev. gén. Caout.* **34**, 363 (1957).
[5] Shutskiĭ, S. V. and Purkin, V. S., 'Viniplast,' a book, Goskhimizdat, (1953).
[6] Bevilacqua, E. M., *J. polym. Sci.*, No. 106, 292 (1957).
[7] Mayo, F. R., *J. Amer. Chem. Soc.* **65**, 2324 (1943).

THE CEPAR (CURE, EXTRUSION, PLASTICITY, AND RECOVERY) APPARATUS *

AN INSTRUMENT FOR MEASURING PROCESSING CHARACTERISTICS OF RUBBER MIXES

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The ease and efficiency with which elastomeric materials may be converted from a raw polymer state to a form ready for vulcanization may be designated by the general term "processability". Since a great many factors enter into processability, such as milling energy required, breakdown time, scorch characteristics, ease of incorporation of pigments, smoothness of formed or extruded articles, and their deformation with time, it is not surprising that a number of different tests have been developed for its evaluation. These tests have been well summarized by R. P. Dinsmore and R. D. Juve[1] who emphasized that the selection of processability test methods must be based on the conditions employed in each specific factory operation. In other words, each of the tests in common use provides information on a limited phase of the problem.

The test described in this paper enables measurements to be made of several of the more important processing variables in a rapid and continuous operation. These include elastic stiffness factor, resistance to orifice flow, hot recovery, flow scorch, and swelling of extruded material.

DESCRIPTION OF APPARATUS AND TEST METHODS DATA PROCESSING

The basic apparatus may be used to perform tests in two distinct categories, evaluation of curing and of processability characteristics of elastomers. Because of its dual use this device has been termed the Cepar (cure, extrusion, plasticity and recovery) apparatus[2]. Only a separate insert in the test chamber is required to change from one type of test to the other.

A sketch of each insert is shown in Figure 1. In the first unit on the left of Figure 1 the extrusion plasticity and recovery insert is shown in the test chamber. Also shown is a portion of the loading arm through which the extruding force is applied.

The second unit on the right of Figure 1 shows the insert for the curing tests. The plunger shown embedded in the test specimen deflects, upon load application, to an extent determined by the state of cure of the specimen.

The scope of the present discussion is limited to the application of the extrusion phase of the Cepar apparatus to the study of processability of elastomers. In this use the Cepar apparatus is essentially an extrusion plastometer operating at a chosen constant relatively low load, with provisions for heating the specimen and for measuring the loading arm deflection at any given time after applying or removing the active load. An extruding force is applied to the test specimen when a load cam is rotated so that the unbalanced beam is

* Reprinted from *Rubber World*, Vol. 143, No. 2, pages 71–83 (1960).

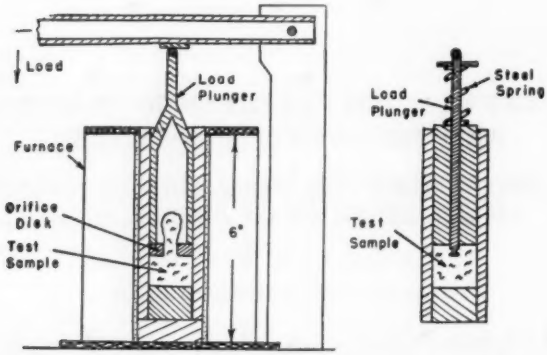

FIG. 1.—Sketch of Cepar apparatus. On the left the extrusion plasticity and recovery insert is in the test chamber. On the right is the insert used for the evaluation of cure characteristics.

lowered on plunger. Cycling timer controls can be adjusted to rotate the cam or to turn on the recorder chart drive with load continuously applied, at intervals of from one minute to 60 minutes as may be desired.

The 3.5- to 4.5-gram test specimen is preformed cold into an approximately cylindrical shape, 0.75-inch diameter by 0.5-inch high to fit into the test cavity shown in Figure 1, *left*. A disk-type slug having a central orifice $\frac{1}{8}$-, $\frac{1}{4}$-, $\frac{3}{8}$-, or $\frac{1}{2}$-inch diameter is loaded on top of the rubber sample, and a chosen load applied. After the sample has been compressed to an initial reference zero (some extrusion occurring thereby), abrupt application of a greater load to the orifice disk causes an instantaneous deflection which is related to the elastic or time independent deformation properties of the material. Continued load application results in a continuous extrusion at a nearly constant rate, the reciprocal of which is a measure of the flow resistance, N_f. Upon removal of the load the extruded portion of the material tends to retract through the orifice, thus forcing the disk upward and providing a measure of hot recovery. After removal of the specimen from the test chamber the diameter or length of

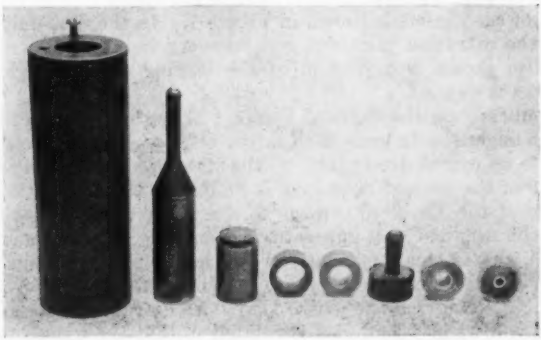

FIG. 2.—Heating cavity unit showing orifice load plunger-specimen assembly.

the extruded portion can be measured. A heating cavity unit with the various inserts and a tested sample is shown in Figure 2.

Each test chamber fits loosely into an electrical heating unit which is controlled individually by a contact relay meter through a thermocouple inserted in the inner chamber wall. Temperature variations at the thermocouple are held to $\pm 1°$ F during normal operation.

A measure of orifice extrusion or of hot recovery is obtained on a strip chart recorder. For this measurement a core of easily magnetized material is suspended from the free end of the loading beam and extended into a motion transmitter coil. Machine constants are such that a plunger motion of 0.1-inch produced 85% of full-scale deflection on the recorder. A motion of 0.1-inch of the $\frac{1}{4}$-inch-diameter orifice disk results in an extruded length of about one inch of the sample specimen. The recorder chart drive may be started automatically when the load is dropped by the rotating cam, or it may be controlled manually through use of a toggle switch provided for this purpose.

An overall view of the four-station apparatus is shown in Figure 3.

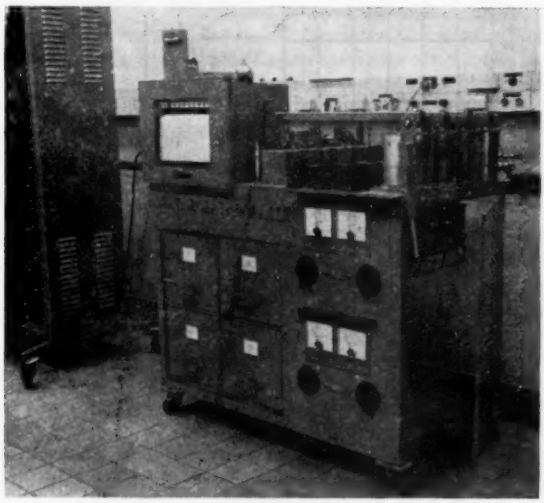

FIG. 3.—Overall view of four-station Cepar apparatus.

Data processing.—A typical chart obtained in the determination of elastic stiffness, M_f, flow resistance, N_f, and hot recovery, R, is reproduced in Figure 4. Elastic stiffness factor, M_f, is a Cepar index related more closely to the recoverable part of orifice flow (deformation flow) than to the non-recoverable (plastic) flow. The horizontal lines in Figure 4 were all obtained while the chart was stopped; those before the time of load removal represent continued flow, and those after load removal represent recovery of the material back through the orifice.

The M_f value is found by dividing the instantaneous deflection into a constant, 845, which is a constant of the Cepar apparatus and equals the number of chart units per inch deflection of the load plunger. For the data in

Figure 4, the instantaneous deflection is given by the length of the horizontal line at the point entitled "load applied". This gives

$$M_f = \frac{845 \text{ chart units/inch}}{(16.4\text{–}12.0) \text{ chart units}} = 192 \text{ inches}^{-1}$$

This is a quantity which is inversely proportional to the near instantaneous "deformation flow" of the sample under conditions of abrupt load application.

The N_f, or flow resistance, value is found by determining the slope of the flow curve at a point where it represents a steady state flow, finding the slope of this angle, and multiplying it by 11.7, which is the ratio of the number of chart units per inch of plunger deflection to chart speed in units per minute.

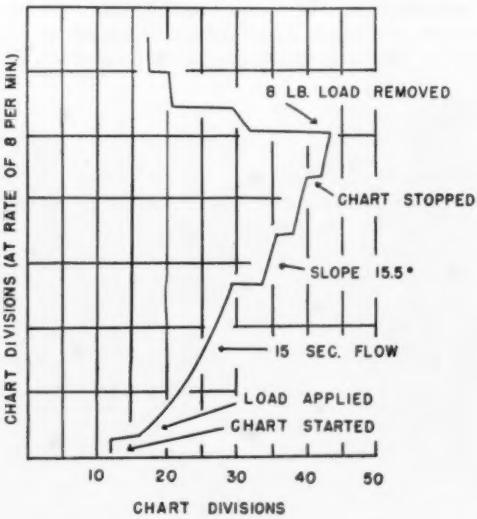

FIG. 4.—Typical Cepar chart for determining M_f, N_f, and R.

For the data in Figure 4 the flow curve near 30 seconds' loading time makes an angle of 15.5 degrees with the direction of chart paper travel, making

$$N_f = 11.7 \text{ cot. } 15.5° = 42.2 \text{ min/inch}$$

This is a quantity which is inversely proportional to the "plastic flow" of the sample. In general, N_f increases with increased loading time due to curing processes. Both N_f and M_f decrease markedly with an increase in driving pressure or an increase in orifice diameter. These conditions, then, must be fixed for tests on stocks which are to be compared with each other.

The hot recovery value, R, is found by dividing the recovery in chart units at a specified time after load removal by the total deformation at the time of load removal. For the data in Figure 4 this gives for the hot recovery index measured one minute after load removal:

Recovery in chart units upon load removal = 43.7 − 21.0 = 22.7 chart units

Total deformation at time of load removal = 43.7 − 12.0 = 31.7 chart units

$$\text{From which } R = \frac{22.7}{31.7} \times 100 = 72\%$$

In a similar manner the recovery could be evaluated for any chosen time after load removal. For many stocks no visible recovery will occur after one minute, whereas others will continue to recover for longer periods. A measure of hot recovery of this nature is believed to be unique among processability tests.

Flow scorch, an increase in resistance to flow due to curing or thermal bonding processes, is found by plotting N_f against heating time. The shape of the curve indicates the scorch behavior of the stock. No specific index for this property has been established, although it has been observed that the heating time represented by the onset of the steep portion of the above curve in general agrees with the scorch time determined by modulus measurements.

Orifice swell is the ratio of extruded diameter to orifice diameter and is determined from measurements made on the specimen after it has been removed from the test chamber and cooled. Normally the specimen tip, which extrudes at a relatively low temperature during the initial loading-preheating period, has a larger diameter than does the portion extruded at a constant rate. Both measurements are usually recorded.

COMPARISON WITH CONVENTIONAL TEST RESULTS

When applied to stocks covering a wide range of plasticities, the conventional plasticity tests and the Cepar test all give results which rate the stocks in the same general order. Considerable differences in relative values are apparent, however, which show the different tests do not all measure the same property. This is illustrated by the data in Table I in which sample C shows the highest Mooney, Williams, N_f and M_f values and recovery indexes of the five cold SBR compound samples in the series. Sample B shows the lowest Cepar recovery and Williams indexes. Indexes for the other samples, however give mixed ratings.

A general correlation between N_f and Firestone extrusion plasticity T-5

TABLE I

COMPARISON OF MOONEY*, WILLIAMS†, AND CEPAR PLASTICITY INDEXES ON COMPOUNDED COLD SBR STOCKS

Compound	A	B	C	D	E
Mooney ML/4/212° F	59.0	51.0	74.5	58.0	56.5
Williams Y_3 @ 212° F (mm)	4.68	4.30	5.60	4.40	4.56
Recovery (mm)	1.16	0.78	2.22	0.91	0.90
Increase (%)	24.8	18.2	39.7	20.7	19.8
Cepar @ 260° F N_f @ 15-sec (min/inch)	25	18	83	33	27
M_f (inch^{-1})	161	84	307	170	143
% Recovery	17	8.6	59.0	21.3	20.0
% Swell (maximum)	24.8	26.0	19.2	24.0	22.4

Cepar test conditions: 260° F, ¼-inch diameter orifice, 8-lb load, 4-g specimens, recovery for 75% load removal (—6 lb).

* ASTM D 1646-59T, American Society for Testing Materials, Philadelphia 3, Pa.

† ASTM D 926-56.

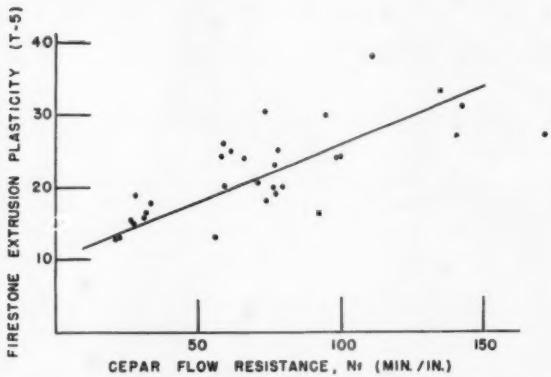

FIG. 5.—Cepar flow resistance vs. Firestone extrusion plasticity index.

values[3] is shown by the data in Figure 5 on a group of cold SBR tread-type compounds.

The time required for a polymer to break down on a mill and the manner in which pigments are incorporated are important characteristics of its general processability. Indexes which have been developed to represent these properties include "knit time", or the time required for the polymer to form a band on the mill, "smooth time", or the time required for the band to become smooth and free from holes, and "carbon black-in time", or the time required for a given amount of carbon black to be incorporated into the mix.

A composite Cepar index, $N_f + \frac{1}{5}M_f$, has been found to vary concomitantly with each of these indexes, as is shown by the data in Figure 6 for a series of samples representing varying degrees of polymerization of an elastomer in a processing study. This composite index was arrived at by a trial-and-error procedure to determine the best relative weighings of the two indexes for correlation with the laboratory mill handling characteristics. The data in

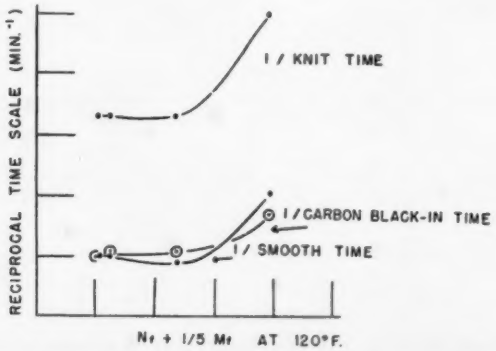

FIG. 6.—Composite Cepar processability index vs. mill handling characteristics of different elastomers. Time scale is in reciprocal minutes.

TABLE II

REPRODUCIBILITY OF CEPAR PROCESSABILITY INDEXES ON A COLD SBR TREAD-TYPE STOCK*

Sample No.	1	2	3	4	5	6	7	8	9	10	Ave.	Statistical Prob-Error
N_f @ ¼-min	18.2	18.2	17.4	19.4	18.2	20.4	18.2	20.9	18.9	20.9	19.1	—
½-min	19.9	19.5	18.9	21.3	20.9	22.4	19.4	20.9	20.9	25.3	20.9	—
¾-min	22.5	20.9	20.9	22.4	21.3	25.3	20.4	23.0	21.8	25.3	22.4	—
1 min	22.5	22.0	21.3	23.6	22.4	25.3	22.4	23.6	23.0	25.7	23.2	± 3.8%
1¼ min	24.2	25.3	23.0	25.3	25.6	25.7	25.3	25.3	23.0	27.3	25.0	—
1½ min	25.3	25.9	24.2	28.0	25.6	28.0	25.3	25.7	23.6	28.0	26.0	—
M_f	—	122	102	—	102	111	101	93.5	102	92.0	108	± 6.3%
R_{15b}† (%)	12.8	12.4	15.0	12.6	13.4	15.1	13.1	15.1	12.9	16	13.8	± 6.0%

Test conditions: 250° F, ¼-inch diameter orifice, 5-g specimens, 6-lb load, 5-min preheat.

* 131 parts oil-extended SBR polymer, 65 parts HAF black; sulfur-N-*tert.*-butyl-2-benzothiazole sulfenamide (Santocure NS, Monsanto Chemical Co.) cure.

† R_{15b} = percentage of total deflection recovered in 15 seconds after removal of 5-lb load.

N_f values given in min/inch. M_f values given in inches^{-1}.

Figure 6 show that the samples of the elastomer which required the shortest time to knit together, to band smooth on the mill, and to incorporate carbon black gave the highest values for the composite index; whereas those requiring the longest times for these phenomena gave the smallest values for the index.

REPRODUCIBILITY OF RESULTS

Reproducibility of the major Cepar processability indexes is generally higher than the reproducibility of different mixes based on a given formula; so they can be used to check the latter.

An illustration of the precision of these indexes is given in Table II where the data represent results obtained on 10 samples of a single mix of cold SBR tread-type stock. The reported probable errors indicate that 50% of all tests made on this stock would give N_f values within ±3.8% of the mean given, M_f values within ±6.3% of the mean, and R values within ±6.0% of the mean. No special precautions were used in mixing this stock.

EFFECT OF TEST TEMPERATURE ON CEPAR INDEXES

Flow resistance, N_f, has always been found to decrease with increasing temperature; however, the recovery, R, and the elastic stiffness factor, M_f, may either decrease or increase with increasing test temperature, depending upon the particular compound and the chosen temperature range. An illustration of the temperature dependence of these Cepar indexes is shown in Figure 7 for a cold SBR compound with 131 parts oil-extended polymer, 65 HAF black; sulfur-Santocure NS cure.

EFFECT OF HEAT HISTORY ON FLOW RESISTANCE

It is well known that fully compounded stocks will "scorch", that is, they will acquire physical characteristics similar to those of partly vulcanized stocks, if they are subjected to sufficiently high temperatures during processing prior to curing for a sufficiently long period of time. Furthermore, such a "heat history", acquired during the various processing stages, is additive. For example, a tread stock batch which is kept in the Banbury mixer for longer than its normal cycle is more likely to scorch in the tread extruder, it has been found, than is a batch which is kept on its normal schedule.

An analogous effect, which cannot be attributed to partial vulcanization,

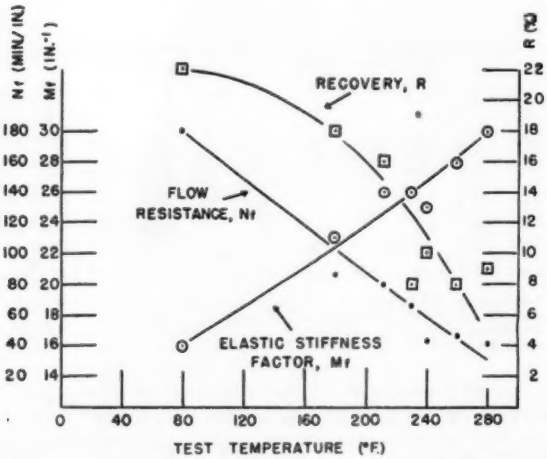

FIG. 7.—Effect of test temperature on Cepar processability indexes for cold SBR tire tread-type stock.

may occur in polymer/carbon black masterbatches. This effect is illustrated in Figure 8 for a masterbatch (no curing ingredients) of 100 parts cold SBR and of 50 parts HAF black, which shows a steady increase in N_f with heating time before testing.

No such effect was found for the raw polymer alone; N_f remained practically constant over a 30-minute heating time at 300° F. Evidently the size of the rheological flow unit in the polymer-black masterbatch became progressively larger as the "heat history" was acquired. Such a picture is consistent with the very large flow units postulated by Mooney[4]. The "thermal bonds" necessary for an increase in size of the flow unit formed quite rapidly at 300° F,

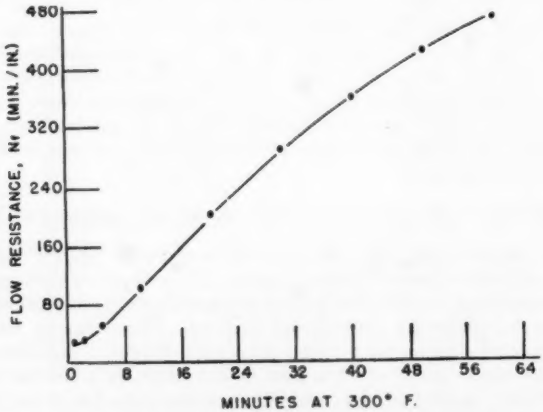

FIG. 8.—Increase in Cepar flow resistance with time at 300° F for a cold SBR-HAF carbon black masterbatch.

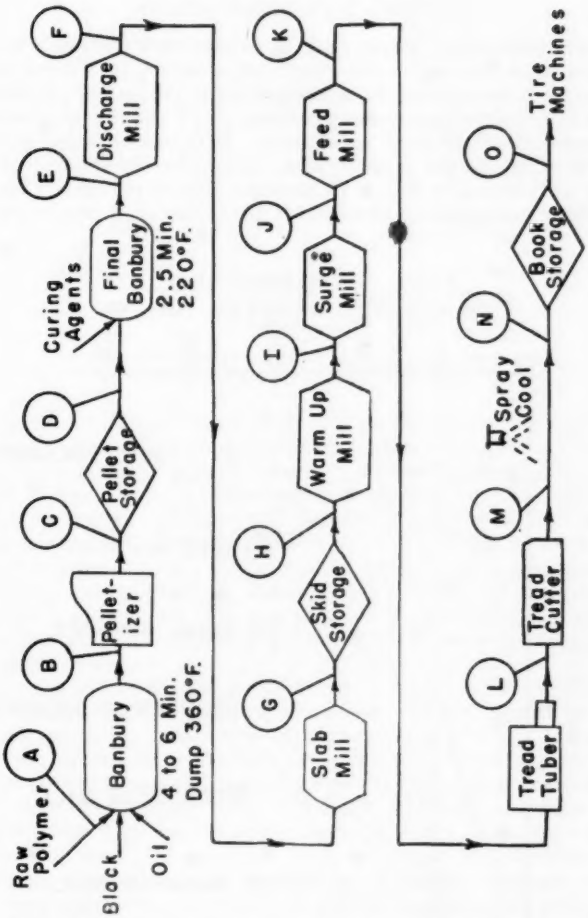

FIG. 9.—Factory tire tread processing stages from raw polymer to tire building machines.

as shown in Figure 8. A subsequent experiment showed that their formation at 280° F, was much slower. After 350 minutes at 280° F, N_f had increased from an initial value of 50 to only 180.

Thermal bonds of the kind shown in Figure 8 did not form at all in compounds containing 50 parts of whiting in place of the black. It was also determined that the thermal bonds formed in the HAF black masterbatch were permanent as regards shelf aging over a period of one month.

Because of the relatively slow rate of formation of these thermal bonds, their effect is masked by the normal curing reaction in fully compounded stocks. Thermal bonds may, however, play an important role in filler stiffening which normally occurs during the first Banbury cycle in factory mixing.

CEPAR TEST APPLICATIONS

A ready application of Cepar methods to heat history effects is in the study of changes in plastic and elastic properties occurring in a tread stock as it progresses from raw polymer to extruded tread in the factory processing cycle. Figures 9 and 10 show the various processing stages and the progressive change in properties for a cold SBR tread stock. Both the softening effect of mechanical working and the stiffening effect of heat history are evident.

Thus, as is shown in Figure 10, incorporation of the carbon black in the first Banbury mixing drastically reduced the orifice swell from about 75% on

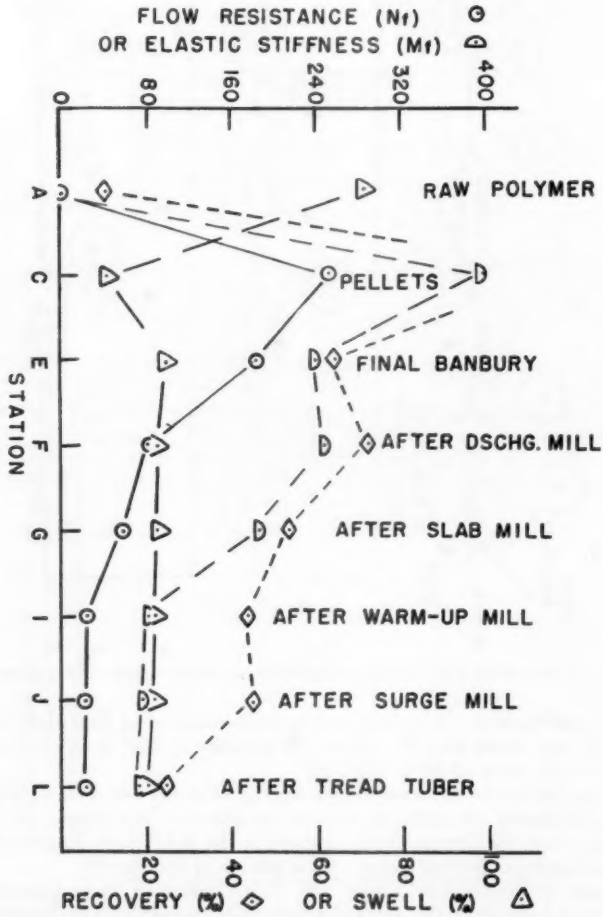

FIG. 10.—Variation in Cepar indexes during factory tire tread processing from raw polymer through tread extruder.

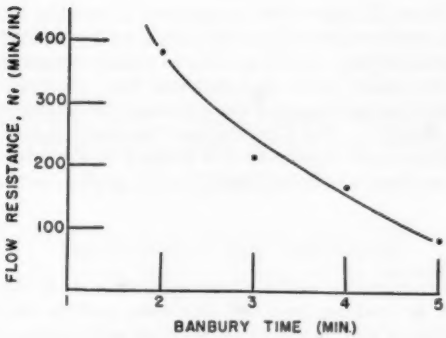

FIG. 11.—Effect of time in the Banbury mixer on the flow resistance of synthetic polyisoprene (Coral rubber).

the raw polymer (station A) to about 15% on the masterbatch (station C). Processing operations after the final Banbury (station E) had very little effect on orifice swell, which is probably due to the counterbalancing effects of the acquisition of heat history by the compound (tending to reduce swell) and of mechanical breakdown of the polymer (tending to increase swell). In general, the Cepar flow resistance, elastic stiffness, and hot recovery of the tread compound were affected in a very similar manner by the various processing stages, as can be seen from the data in Figure 10. The discharge mill (station F); however, has a considerable softening effect on the compound as regards flow resistance, but the elastic stiffness and hot recovery were scarcely altered by this processing operation.

Another example of the use of the Cepar apparatus is shown in Figure 11, where the results of the progressive breakdown of Coral rubber (Firestone's synthetic polyisoprene) in the size B Banbury mixer are shown. The apparatus was well adapted to this study since the small test sample required made it convenient to take samples from the Banbury at one-minute intervals.

In another compounding study it was required that the stock involved should have a very high durometer hardness and that it should have very little flow while being cured. It was soon established that such a stock was too stiff to evaluate on conventional test equipment. A special test based on the use of the Cepar apparatus, however, did provide the required data. It was determined that the total length of the stock extruded during a seven-minute period at 300° F should be not more than 0.40 inch. Some of the compounds evaluated were air-curing, and it was necessary to determine the effect of storage between mixing and curing.

TABLE III

CEPAR EVALUATION OF AIR CURING HIGH HARDNESS COMPOUNDS

No. days between mixing and testing	Inches 7-min extrusion—various compounds					
	F	G	H	I	J	K
3	.38	.37	.25	.29	.27	.68
11	.28	.31	.18	.26	.19	.44

Cepar test conditions: ⅛ in. diam orifice, 300° F, 5-g sample, 2-lb load @ ¼ min, + 11 lb @ 1¼-min. Load removed @ 7 min.

The data in Table III show that compound K was the only one of the six compounds which were evaluated that did not meet the extrusion requirement. Since curing progressed very rapidly as soon as curing temperature was reached, the stocks were in a cured state upon removal from the apparatus at the end of the seven-minute period, most of the extrusion having occurred during the first two or three minutes. The Cepar apparatus could be used advantageously in this study because ready access to the interior of the heating chamber was possible, and no problem was encountered by the stocks "setting up" or curing during the test.

SUMMARY AND CONCLUSIONS

The principal advantages of the Cepar apparatus over commercially available plastometers for making processability tests include the following: small sample size; rapidity of testing; the wide range of orifice sizes, driving pressures (loads), and temperatures readily available; versatile controls for incremental extrusions at timed intervals (for studying curing effects) and/or for continuous extrusions; and the feasibility of using this apparatus to evaluate flow characteristics of stiff or "boardy" compounds or even of cured compounds normally considered out of range for conventional tests. The apparatus, in its normal application, will yield values for instantaneous orifice deflection (elastic stiffness factor), the continued rate of extrusion, and hot recovery upon load removal. Tests can also be made upon the removed sample for such things as orifice swell, extruded length, etc.

In addition to the applications cited in this paper, the apparatus has been used to study the problem of knitting of factory stocks, as a control instrument to select the best temperature for extrusion processes, and as an evaluation instrument for various compounding studies. It has been used also as an instrument to evaluate the degree of heat softening (up to temperatures of 600° F) occurring in high-temperature heat-resistant stocks, in studies correlating factory extruded tread center gage with Cepar swell measurements, and in tests for degree of polymerization in SBR produced by the continuous process.

ACKNOWLEDGMENTS

A great many members of Firestone research organizations contributed toward the development and evaluation of the Cepar apparatus in demonstrating its range of application. In this connection we especially want to thank Sydney Smith and the Firestone research laboratory physical testing group. The continued interest and encouragement of F. W. Stavely and J. W. Liska are especially acknowledged. The permission of the Firestone Tire & Rubber Co. to publish the work is also greatly appreciated.

REFERENCES

[1] Dinsmore, R. P. and Juve, R. D. in "Synthetic Rubber," edited by G. S. Whitby, C. C. Davis and R. F Dunbrook, pages 381–382, John Wiley & Sons, Inc., New York, 1954.
[2] Claxton, W. E., U.S. 2,904,994 (Sept. 22, 1959).
[3] Dillon, J. H. and Johnston, N., RUBBER CHEM. & TECHNOL. 7, 248 (1934).
[4] Mooney, M., *J. Appl. Phys.* 27, 691 (1956).

EVALUATION OF PROGRESSIVE CHANGES IN ELASTOMER PROPERTIES DURING VULCANIZATION *

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INTRODUCTION

Evaluations of state of cure and of rate of cure in elastomers have been the subject of a great number of investigations reported in rubber literature. These have resulted in the development of a number of test methods, which have been well summarized by Juve[1]. The most commonly used test is a highly subjective combination of tensile modulus, ultimate elongation and rupture strength, although it has been pointed out by Schade[2] that experienced compounders may reach a wide range of "optimum" cures, all based on a given set of data. A greater precision has been claimed by Schade and by Stiehler and Roth[3, 4] for a dead weight strain test method for evaluating cure. A nearly absolute measure of degree of vulcanization by a swelling method is claimed by Kraus[5].

In a method described by Peter and Heidmann[6] and by Payne[7] a dynamic shear modulus is measured during the progress of vulcanization and reversion thus obtaining a complete curve of modulus vs. cure time on a single specimen.

A similar method is used in the recently marketed Wallace-Shawbury Curometer[8, 9]. One drawback to this method is that the specimen cures under no hydrostatic pressure, resulting in variable porosity. In all of the methods described in Reference 1 it is necessary to cure specimens to each of the states for which data are desired and then run the appropriate physical test, which procedure consumes a great deal of both time and sample material.

It is often advantageous to know certain curing parameters besides the time for "optimum" cure. Stiehler and Roth[3] decided that three parameters are necessary to describe curing properties (a) scorch time, (b) rate of cure, and (c) a structural factor which may be associated with the inherent stiffness of the rubber compound. In one series of tests they obtained all of these factors on their strain tester. In another series they used a Mooney Viscometer for evaluating scorch time. Gee and Morrell[10], among others, preferred to use the Mooney instrument for scorch time, while depending upon modulus tests for cure rate and state of cure. Juve[11] has suggested a method for obtaining optimum cure times as well as scorch times from the Mooney Viscometer. The advantage of a single instrument and test procedure for determining all of the desired parameters is obvious.

The test described below yields objective indexes for: (a) scorch time (first observable stiffening), (b) induction time (extrapolation of curve to zero cure), (c) curing rate, (d) time for attainment of any specified percentage of full cure,

* Presented before the Division of Rubber Chemistry, ACS, New York, N. Y., Sept. 15, 1960. Reprinted from *Rubber World* 144, 71–78, (1961).

(e) induction time for start of reversion, (f) reversion rate and (g) time for reversion to cause any specified percentage loss in the fully cured modulus. The method is based on measurements of progressive modulus change during cure, following Fletcher, Gee and Morrell[12] in the use of modulus as a measure of the state of cure.

It was shown in an earlier work[13] that the state of cure of an elastomer could be represented by the ratio of a Young's modulus M at cure time T to the corresponding modulus M_∞ at full cure, and that this ratio could be represented adequately by an equation derived from a first order reaction hypothesis,

$$M/M_\infty = 1 - e^{-k(T-T0)}$$

wherein k is a curing rate constant and T_0 is the induction period, or cure time before the modulus starts increasing significantly, and $e = 2.72$ is the natural logarithm base. Stiehler and Roth[3] maintain that a second order cure reaction theory agrees with facts better than does a first order reaction. The above equation, however, was found to apply to all of the compounds investigated within the limits of compound reproducibility.

DESCRIPTION OF APPARATUS

In addition to its use in determining cure parameters, the test apparatus was designed for processability evaluations on polymers and unvulcanized compounds. In order to indicate its complete range of utility it has been termed the Cepar apparatus[14] (cure, extrusion plasticity and recovery). Its use in plasticity determinations is described in a separate report[15], in which an overall description of the apparatus is also given.

The apparatus in present use (Figure 1) is a 4-station model with individual temperature controls for each station and a common chart recorder for all stations. Components of the test chamber are shown in the photograph of Figure 2. In Figure 3 the test specimen is shown confined in a $\frac{3}{4}$ inch diameter chamber which is heated to the desired temperature by the surrounding electric furnace. Test temperatures are controlled roughly by a manually set auto-

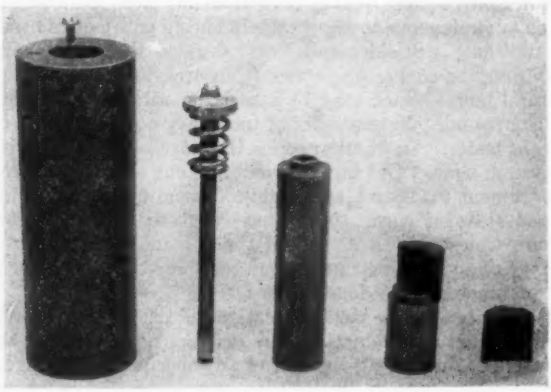

FIG. 2.

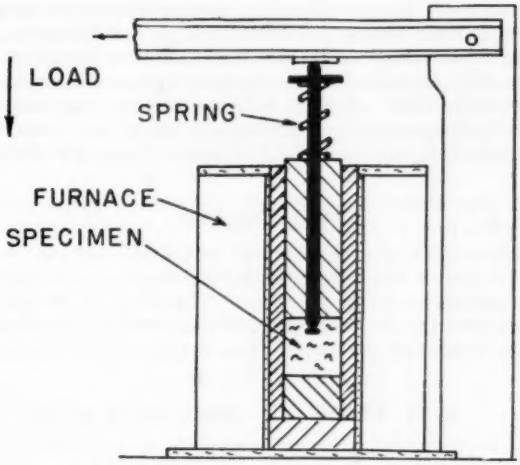

FIG. 3.

transformer on the furnace windings and more precisely by a contact relay meter which is actuated by a thermocouple inserted in the hole shown in the test chamber wall (Figure 2). The latter controls about ½ of the applied voltage. By this method the temperature of each unit may be controlled individually within ±1° F in the range of 77° F to 600° F.

A dead weight is applied periodically to the ¼ inch diameter loading plunger by motorized rotation of the cam at predetermined intervals of from 1 minute to 1 hour. The load is sufficient to produce a unidirectional compression of about 8% in the uncured specimen, the displaced rubber moving upward against the force of a coil spring. The loading pressure of about 50 psi applied to the specimen to force the loading beam down to the cam is sufficient to force the plunger tip into the rubber where it remains embedded during the cure. It is also sufficient to produce a non-porous vulcanizate. The load to be used is selected so as to give nearly full scale recorded deflection on the uncured specimen.

The deflection sensing device is a differential transformer, the core of which is link-corrected to the end of the loading beam. Deflections are recorded on a roll chart recorder, the chart drive of which is started automatically one second before the rotating cam allows the full load to be applied to the specimen and is stopped automatically after an on period of three seconds.

TEST METHOD

Test specimens of raw rubber were either weighed or preformed by extrusion to an essentially constant volume. For normally compounded SBR or natural rubber 4.2 g was satisfactory, gum stocks required slightly less and highly pigmented stocks slightly more. Samples were preformed cold in a pressure mold to approximately a cylindrical shape ¾ inch in diameter by ½ inch high.

With the heating chamber at the desired temperature and load cycling controls set to proper times, the specimen is inserted at a noted time, and the

load applied with the cam positioned to support the major load. Approximately 30 seconds later the cam is rotated to apply the full load to the loading plunger, giving a short trace of the resulting deflection on the recorder chart. Deflections on the succeeding drops increase slightly or remain constant at first as the sample heats up, then decrease continuously during the cure. Usually there is a comparatively long interval after full cure is attained wherein deflections remain fairly constant. As reversion begins the deflections again increase.

DATA ANALYSIS

A reproduction of a typical chart record for a single unit is given in Figure 4. A smooth curve drawn through the deflection maxima shows the progress of both the cure and the reversion processes. The scorch time, indicated by R_s, is the time required for the first observable stiffening. The induction time, R_0, is found by extending the straight line portion of the cure curve until it

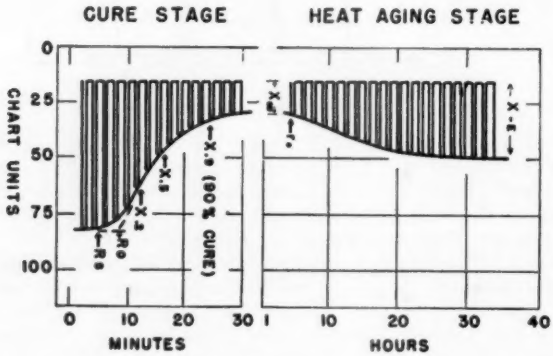

FIG. 4.

reaches the zero cure level. The term R_0 will be recognized as the Cepar measure of the more general term T_0 which appeared in the preceding equation. The time to reach a "practical" 100% cure can be read directly from the chart. Additional significant parameters can also be obtained from the data. Consider the following relations.

Let K = the fractional modulus change of a stock completed after any given curing time

M = Modulus at fractional change K

M_i = initial modulus of uncured stock

M_∞ = modulus of fully cured stock

then

$$K = \frac{M - M_i}{M_\infty - M_i} \quad \text{or} \quad K = \frac{\dfrac{M}{M_\infty} - \dfrac{M_i}{M_\infty}}{1 - \dfrac{M_i}{M_\infty}}$$

since we have taken modulus change as a measure of state of cure. In the latter form it is seen that if M_i/M_∞ (the initial cure) is small as compared with unity, the value of K at any cure time is a measure of the difference in fractional modulus cure that has occurred in the stock. Normally any stock that can be preformed satisfactorily for testing in the apparatus will be at a very low state of cure ($M_i/M_\infty \sim .01$); hence, except for very low cures, the value of K as given above will be essentially equal to M/M_∞, our previous definition for state of cure.

The modulus terms in the above expression should be converted into deflection terms for application to a chart record such as that in Figure 4.

Let X = chart deflection at fractional cure K
X_i = initial chart deflection
X_∞ = chart deflection of fully cured stock

making

$$K = \frac{X_i - X}{X} \Big/ \frac{X_i - X_\infty}{X_\infty}$$

since the force is the same at all deflections.

The above equation may be solved for X, giving

$$X = X_i \left[1 + K\left(\frac{X_i}{X_\infty} - 1\right)\right]^{-1}$$

For a 20% cure, for example

$$X_{.2} = X_i \left[1 + .2\left(\frac{X_i}{X_\infty} - 1\right)\right]^{-1}$$

With the deflection for a given state of cure thus determined, the cure time can be read directly from the chart. Use of the chart deflection measurements in this manner avoids the necessity of calculating an absolute Young's modulus since only the relative values are required. A 90% cure has been used satisfactorily as "optimum".

The curing rate constant k evaluated from the induction period T_0 and the time T required to reach a fractional modulus K is given by:

$$k = (T - T_0)^{-1} \ln [1/(1 - K)]$$

Heat degradation measurements may be analyzed in an analogous manner. Let X_{-p} represent the chart deflection level after a given cure time which has caused a modulus reduction to a fraction P of the undegenerated modulus, then

$$P = \frac{X_i - X_{-p}}{X_{-p}} \Big/ \frac{X_i - X_\infty}{X_\infty}$$

and

$$X_{-p} = X_i \left[1 + P\left(\frac{X_i}{X} - 1\right)\right]^{-1}$$

The degradation reaction rate constant evaluated from the time r_q, meas-

TABLE I

STATE OF CURE AS DETERMINED BY THE CEPAR TEST AND BY TENSILE MODULUS DATA. LTP TREAD STOCK. 280° F CURING TEMPERATURE

Cure time from Cepar		From ring sample (Cepar specimen) (% cure)		From dumbbell sample (% cure)
(Min)	(% Cure)	100% Ext.	300% Ext.	300% Ext.
15	50	53	55	53
30	81	83	86	80
45	95	96	99	97
60	~100	~100	~100	~100

ured from the beginning of the cure run, that is required before the degradation reaction is $q \times 100\%$ complete is given by:

$$\gamma = (r_q - r_0)^{-1} \ln [1/(1 - q)],$$

where r_0 is the time at which the heat aging reaction commenced.

COMPARISON OF RESULTS WITH CONVENTIONAL PHYSICAL TEST DATA

State of cure as evaluated by the Cepar apparatus is in good agreement with that determined from tensile modulus tests, as is shown by the data in Table I. For the LTP (low-temperature SBR) tread stock tested it had been shown that a 60 minute cure produced very close to the maximum modulus attainable. The degree of cure produced by each of the shorter curing times was determined from the percentage of this maximum modulus attained from both the Cepar and physical testing data.

The ring sample on which data are given in Table I was molded on the bottom of the Cepar specimen and cut off by a razor blade on a lathe. By this procedure a tensile test specimen is obtained which has exactly the same state of cure as the final state of the Cepar specimen itself. Other physical measurements may be made on the cured Cepar cylinder. These include compression modulus (ratio of compressive stress to linear compression) recovery, hardness, resilience and specific gravity. A very satisfactory compression modulus measurement can be made on the Cepar apparatus itself by placing the cured Cepar cylinder on a separate support under one of the loading arms and using the recorder to measure the resulting deflection. It is thus possible to obtain both Cepar and a variety of physical testing data on as little as 5 grams of sample—a definite advantage when evaluating experimental polymers.

In one model of the Cepar apparatus the loading beam was extended past a knife edge pivot to form a nearly balanced double beam, which was loaded

TABLE II

SCORCH TIME AS DETERMINED BY THE CEPAR TEST AND BY THE MOONEY PLASTOMETER. HEVEA TREAD TYPE STOCK

Remill time (min @ 240° F)	Cepar scorch time (min @ 250° F)	Mooney scorch time (min @ 250° F)
0	32.5	25
2	27.5	27
6	21	24
10	17.5	18
20	7.5	7

TABLE III

REPRODUCIBILITY DATA ON 4-UNIT CEPAR APPARATUS HEVEA TREAD COMPOUND, 280° F TEST TEMP., 4.2 g SAMPLE 4.5 LB LOAD. 1¼ MIN CYCLE

Induction period R_0 (min)					Time to 50% cure $R_{.5}$ (min)				
Run No.	Unit 1	2	3	4	Run No.	Unit 1	2	3	4
1	9.0	7.7	8.3	9.7	1	16	15	16	15
2	11	9.6	7.8	9.7	2	15	17	14	15
3	10	11	10	9.7	3	17	17	17	16
4	9.5	9.7	9.3	8.6	4	15	17	16	14
5	9.6	9.0	9.4	9.7	5	15	15	16	15
6	9.1	8.9	7.8	8.4	6	15	16	14	12
Ave. R_0 = 9.3 min.					Ave. $R_{.5}$ = 15.5 min.				

Time to 90% cure $R_{.9}$ (min)					Cure rate constant k (min^{-1})				
Run No.	Unit 1	2	3	4	Run No.	Unit 1	2	3	4
1	33	32	34	29	1	.095	.095	.088	.12
2	27	36	29	29	2	.14	.087	.11	.12
3	32	30	32	31	3	.10	.12	.10	.11
4	33	34	33	28	4	.13	.095	.096	.12
5	29	33	33	26	5	.12	.095	.099	.14
6	30	32	27	21	6	.11	.10	.12	.19
Ave. $R_{.9}$ = 30.5 min.					Ave. k = .11 min^{-1}				

sufficiently to produce a natural period of oscillation, with the rubber sample in position, of about .75 cps. When the load supplied by the beam unbalance was applied suddenly to the loading plunger damped oscillations were obtained which could be interpreted much as for the Yerzley oscillograph. The progressive change in dynamic properties during cure thus obtained showed that, for most stocks, resilience increased monotonically with increase in cure.

TABLE IV

ANALYSIS OF VARIANCE SHOWN BY DATA IN TABLE III*

	Degrees of freedom	Mean square	Standard deviation
Induction period R_0			
Between units	(3)	1.24	Insignificant
Between runs	5	1.70	0.5 min
Residual error	15+(3)	.726	0.9 min
Time to 50% cure $R_{.5}$			
Between units	(3)	.72	Insignificant
Between runs	(5)	2.45	Insignificant
Residual error	15+(3)+(5)	1.48	1.2 min
Time to 90% cure $R_{.9}$			
Between units	3	32.4	2.0 min
Between runs	(5)	11.3	Insignificant
Residual error	15+(5)	7.5	2.6 min
Curing rate constant k			
Between units	3	.00149	.014 min^{-1}
Between runs	(5)	.00041	Insignificant
Residual error	15+(5)	.00036	.019 min^{-1}

* Reference 16.

TABLE V

EFFECT OF FREQUENCY OF LOAD APPLICATION ON MEASURED CURE PARAMETERS OF A NATURAL RUBBER TREAD TYPE COMPOUND

Load cycle (min)	R_0 (min)	$R_{.5}$ (min)	$R_{.9}$ (min)	k (min^{-1})
1.25	9.3	15.5	30.5	.11
2.5	10.5	16.8	32.8	.11
5	10.0	17.0	33.0	.10

Conditions: 280° F, 4.2 g samples, 4.5 lb load.

The dynamic properties, however, lagged behind the static properties. In some cases the most resilient cure was definitely overcured by the normal Cepar index. Resilience measurements could be obtained on this version of the apparatus either with the specimen in the curing chamber or positioned as for the compression modulus test mentioned above.

The Cepar scorch time shows good agreement with that obtained on the Mooney plastometer. This is illustrated in Table II for a Hevea tread type compound. The progressively shorter scorch times were obtained by remilling the stock for the indicated times.

Reproducibility of results.—During the trial runs on the 4-station apparatus a study was made of the reproducibility between units and between runs. As is shown in Tables III and IV both of these variations were smaller than the residual error. The only significant between runs variance found was in the induction period. Since this parameter was measured rather early in the cure cycle, it may have been affected by unequal cooling of the heating chambers during the specimen insertion. This source of error has been reduced by insertion at the top rather than the bottom of the chamber, whereby it is unnecessary to remove the chamber from the furnace.

The between units variation in curing rate constant and time to 90% cure shown in Table IV was traced to unit # 4 which appeared to be operating somewhat hotter than did the other units. This difficulty has been corrected simply by closer attention to proper setting of the controls.

Values found for the various curing parameters are not influenced appreciably by the frequency of load application during the test, as is shown by the data in Table V. The choice of load cycle to be used is usually based on the expected curing rate of the test specimen. A fast curing stock would be tested at a high loading frequency in order to provide a sufficient number of chart readings for a smooth curve to be drawn.

TABLE VI

EFFECT OF STATE OF CURE ON VARIOUS PHYSICAL PROPERTIES OF HEVEA SIDEWALL TYPE STOCK

	Undercure		Normal cure		Overcure		
Cure time @ 280° F	16.5′	22.5′	35′	50′	3 hr	4.5 hr	14 hr
fractional modulus (K)	0.5	0.7	0.9	1.0	−0.9	−0.8	−0.7
1. Normal stress-strain (ASTM D412)	Poor		Good		Poor		
2. 2 days oven aging @ 212° F (ASTM D573)	Good		Fair		Poor		
3. 96 hr oxygen bomb aging (ASTM D572)	Fair		Good		Fair		
4. Hysteresis (Firestone Shear Vibrometer)	Poor		Good		Poor		
5. Sidewall flexing	Good		Poor		Good		
6. Crack initiation	Fair		Poor		Good		
7. Oxygen absorption	Good		Fair		Poor		
8. Ozone resistance (ASTM D1149)	Fair		Good		Fair		

Use as a screening test.—In many compounding studies it is desirable to be able to evaluate a large number of ingredients which may affect the cure in an unknown manner. Some might accelerate the cure to such a degree that the shortest time used in a conventional tensile test would produce an overcure, while others might be extremely slow curing. In either case an appreciable saving in testing time could be determined approximately by a preliminary screening test. For this need the Cepar test has been found to be very satisfactory, especially when dealing with experimental polymers or compounding ingredients in short supply.

Optimum cure for one physical property may not always be optimum for another property. For example, life in a sidewall flexing apparatus was found to be longer for undercures ($K \sim 0.5$) or overcures ($K \sim -0.7$) than for "normal" cures ($K = 0.9$ to 1.0). On the other hand, hysteresis properties were best for normal cures and became sharply poorer for both undercured and overcured states. A summary of the effect of state of cure on eight physical properties of a Hevea stock is given in Table VI.

In the evaluation of rubber chemicals the appropriate physical tests should be made on vulcanizate samples which have been cured to a given state. In the region of flat cure, where stress-strain properties are nearly constant, significant variations in other properties may occur which would affect the evaluation of the ingredient being tested.

TABLE VII

CEPAR SCORCH ON STIFF COMPOUNDS

Compound	Scorch time (min @ 250° F)
Hevea Pale Crepe	23
Pale Crepe + 20% Pre-vulcanized latex	17.5
Pale Crepe + 35% Pre-vulcanized latex	7.3
Pale Crepe + 50% Pre-vulcanized latex	5

Use on very stiff compounds.—Some experimental compounds are too stiff to be tested for scorch on the Mooney plastomer. In general, however, this index can be obtained on the Cepar apparatus. An illustration is given in Table VII showing how increasing amounts of prevulcanized latex decreased the scorch time of a pale crepe natural rubber compound.

Use as a millroom control instrument.—Millroom control tests are made on each batch of factory stock as a check on proper compounding. Normally these tests are limited to specific gravity determinations and modulus tests on a single cure, thus giving very little information about any stock that might be outside the control limits on these properties. The Cepar test is capable of yielding the required basic information with a minimum of test time, plus additional important information regarding both curing characteristics and physical properties of the vulcanizate. By a simple test chamber substitution it is also possible to evaluate quickly a number of extrusion properties.

As an illustration of this type of use consider the data shown in Table VIII. Assuming that these specimens were a representative set the mean values and probable errors shown at the bottom of the table were calculated. With these data as a basis a transparent overlay template shown in Figure 5 was prepared. The central dotted curve represents the average cure curve for the 15 samplings. The lower line is the slowest cure rate, the longest induction period and the smallest initial-final deflection difference allowable. The upper line is the

TABLE VIII

CEPAR DATA ON 15 BATCHES OF AN LTP TREAD TYPE COMPOUND

Sample No.	Induction Period R_0 (min)	Curing rate k (min^{-1})	Initial-final chart deflection (chart units)	Compression modulus (psi)	Specific gravity
1	3.68	.500	29.5	565	1.150
2	3.48	.480	32.3	505	1.155
3	3.73	.342	35.2	485	1.150
4	3.45	.400	33.0	585	1.150
5	3.32	.380	34.6	533	1.150
6	3.68	.380	32.0	524	1.150
7	3.98	.390	35.2	520	1.148
8	3.79	.420	34.0	475	1.145
9	3.78	.425	35.5	555	1.148
10	4.62	.460	37.6	680	1.155
11	4.12	.403	31.4	610	1.155
12	4.22	.400	34.4	550	1.155
13	4.02	.380	35.0	645	1.155
14	4.88	.318	30.5	532	1.150
15	4.57	.380	34.0	545	1.155
Average	3.92	.404	33.7	555	—
Probable error	±0.3 (±8%)	±.032 (±8%)	±1.31 (±3%)	±36 (±6.5%)	

Conditions: 328° F cure, 4.2 g specimens, 4.5 lb load, 1 min cycles, samples cured 14.5 min.

fastest cure rate, the shortest induction period and the largest initial-final deflection difference allowable. In using this template the arrow is placed on the chart to coincide with the 30 second reading of the specimen deflection under load. The template is then aligned with the chart paper and the cure curve observed to fall within or without the chosen ranges. In using this template alone as a control criterion it would be necessary to allow the cure to proceed only long enough to determine whether or not it was within the prescribed limits.

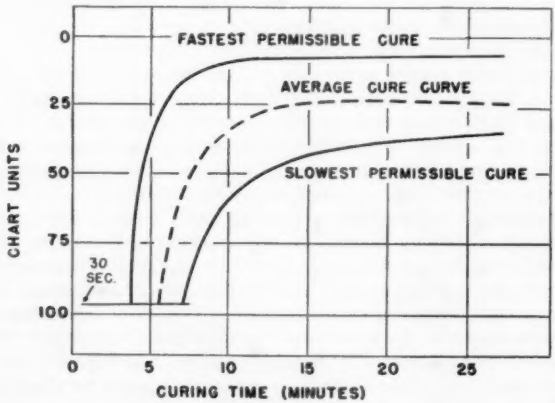

FIG. 5.

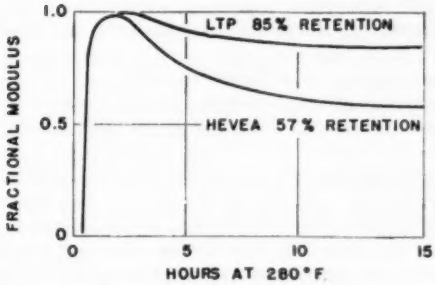

Fig. 6.

The above method gives three parameters by which the stock might be rejected—the induction period, the cure rate and the extent of cure; whereas the conventional millroom control tests give only one—the modulus at a given cure time. Consider, for example, a stock which had been given a double measure of curing agent or accelerator. It could well be within modulus limits, but on the reversion side of the cure curve. Such a batch could pass the normal millroom control test and cause much difficulty in further processing stages. The Cepar apparatus cure curve would, however, reject every such batch.

If physical testing data on the vulcanizate are desired, compression modulus and specific gravity data as shown in Table VIII may be obtained on the cured Cepar specimen, or tensile data may be obtained on the ring cut from the bottom of the specimen as previously described.

Use in measuring reversion.—An elastomer which is kept confined at curing temperature for prolonged periods will usually show a heat effect wherein the modulus begins to decrease at a particular time, proceeds exponentially and eventually levels off. Typical modulus changes during the cure and heat degradation of a Hevea compound and of an LTP compound, as shown by the Cepar apparatus, are shown in Figure 6. Although modulus retention has not been investigated thoroughly, it may be a factor in tread wear[17]. Modulus retention factors (P), measured after the modulus had leveled off, ranging from 38% to 92% have been measured on Hevea tread type compounds in which the accelerator had been varied. Such a wide range of values should be reflected in any service application where additional heat history is acquired.

Induction times required for reversion to start may also vary widely. A range of from 12 min. to 100 min. was observed, for example, in a series of Hevea and Hevea/LTP blends. Reaction rates for reversion on the same compounds ranged from 0.007 to 0.045 min.$^{-1}$. These measurements represent physical properties to which little attention has been given in the literature.

DISCUSSION

The Cepar modulus test for cure differs from conventional tests in several respects. The differences might appear at first impression to make it incomparable with them. They involve the features that (a) the Cepar test is made at curing temperature rather than room temperature, (b) no rest period between curing and testing with the Cepar test is possible, (c) Cepar

deflections are small, about 8% unilateral compression, (d) Cepar cures are made under pressures (about 50 psi) considerably less than those normally used on physical testing samples, and (e) the first deflection measurements with the Cepar test may be made before the specimen has reached equilibrium temperature (it requires about 4 minutes for the interior of the specimen to attain 98% of the differential between room temperature and the curing temperature).

It should be pointed out in view of the above points that no attempt is made to measure absolute modulus in the Cepar test, but only the relative change in modulus between the uncured and the fully cured specimen. It has been shown, as by the data in Table I, that this method yields a value for degree of cure that is in agreement with that obtained by more conventional methods. In regard to item (d) above, it was found during developmental work on the apparatus that a weak spring holding the plunger in the specimen did indeed cause a porous vulcanizate. This condition was eliminated by substituting a stiffer spring. No significant effect of curing pressure within the normal range used has been found, provided that it is sufficient to prevent sample porosity.

In regard to item (e) above, it is necessary to disregard plunger deflection readings obtained before the maximum deflection is reached, at which time the specimen may be regarded as having reached thermal equilibrium. This in no way interferes with the measurements. Curing time is regarded as starting at the instant the specimen is inserted into the hot curing chamber.

SUMMARY AND CONCLUSIONS

An apparatus and method are described for evaluating state of cure, optimum cure time, rate of cure, induction time for cure, scorch time, induction time for reversion, reversion rate and degree of reversion of elastomeric compounds. Coincident with these determinations vulcanizate specimens are prepared on which more conventional physical test data may be obtained; e.g., compression modulus, compression set, hardness, specific gravity, tensile modulus and elongation.

In essence, the method described provides a progressive measure of modulus change during cure or reversion through the change in deformation of a periodically loaded plunger, one end of which is embedded into the specimen. Typical results are given which show application of the apparatus to screening tests, millroom control, reversion studies and to compounds which are too stiff for conventional test methods.

Demonstrated advantages for the apparatus include time saving, stock saving and better cure information on a wider range of polymeric compounds than is obtainable from tensile test methods. In a laboratory where a large selection of test instruments is not feasible, the versatility of the apparatus described should prove very advantageous.

ACKNOWLEDGMENTS

A great many members of the Firestone Research organization contributed toward the development and evaluation of the Cepar apparatus, especially in demonstrating its range of application. The continued interest and encouragement of Dr. F. W. Stavely is especially acknowledged as are the helpful

suggestions made by Sydney Smith. The permission of The Firestone Tire and Rubber Company to publish the work is greatly appreciated.

REFERENCES

[1] Juve, A. E., in "Synthetic Rubber" edited by G. S. Whitby, C. C. Davis and R. F. Dunbrook, p. 425, John Wiley and Sons, Inc., New York, 1954.
[2] Schade, James W., *India Rubber World* **123**, 311 (1950).
[3] Stiehler, R. D. and Roth, F. L., Special Publ. No. 138 of the American Society for Testing Materials; RUBBER CHEM & TECHNOL. **26**, 593 (1953).
[4] Roth, F. L. and Stiehler, R. D., *India Rubber World* **118**, 367 (1948); RUBBER CHEM. & TECHNOL. **22**, 201 (1949).
[5] Kraus, Gerald, *Rubber World* **135**, 67, 254 (1956).
[6] Peter, J. and Heidemann, W., *Kautschuk und Gummi* **10**, 168 (1957); RUBBER CHEM. & TECHNOL. **31**, 105 (1958).
[7] Payne, A. R., *Rubber Journal and International Plastics* **134**, 915 (1958).
[8] Anon. *Rubber Age* **86**, 1074 (1960).
[9] More, A. R., Morrell, S. H. and Payne, A. R., *Rubber Journal and International Plastics* **136**, 858 (1959)
[10] Gee, Geoffrey and Morrell, S. H., *Trans. Inst. Rubber Ind.* **28**, 102 (1952).
[11] Juve, A. E., *Rubber World* **140**, 705 (1959).
[12] Fletcher, W. P., Gee, Geoffrey, and Morrell, S. H., *Trans. Inst. Rubber Ind.* **28**, 85 (1952).
[13] Claxton, W. E., *J. App. Phys.* **29**, 1398 (1958).
[14] Claxton, W. E., U. S. 2,904,994 (1959).
[15] Conant, F. S. and Claxton, W. E., *Rubber World* **143**, 71 (1960); preceding paper, this issue.
[16] Davis, O. L., "Design and Analysis of Industrial Experiments," Chap. 5, Hafner Publishing Co., New York, N. Y. 1956.
[17] Van Amerongen, G. J., *Ind. Eng. Chem.* **47**, 2565 (1955).

SIMPLE ROTARY DYNAMIC TESTING MACHINE *

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INTRODUCTION

Kimball and Lovell[2] measured energy dissipation during cyclic deformation, using a test piece in the form of a cantilever rotated about its axis. The method has recently been applied by Maxwell[3, 4] to the study of the viscoelastic behavior of polymethyl methacrylate ("Perspex"), because it enables the dynamic mechanical properties to be evaluated very simply for a wide range of deformation frequencies. It has two disadvantages, however. Firstly, the testpiece is not uniformly deformed; in fact, the largest strains are imposed in the neighborhood of the clamped or bonded faces and, hence, are particularly susceptible to inadequate fastening arrangements. The nonuniformity of strain is also undesirable when examining materials which show a nonlinear dependence of their viscoelastic reactions on the strain amplitude. Secondly, the examination of soft materials (for example, vulcanized rubbers) is not easily accomplished, because the test specimen consists of a long thin rod which may be unable to support its own weight statically, and will whirl or whip at relatively low frequencies of rotation. A test machine has therefore been devised, and is described below, which imposes a homogeneous deformation on a rotating testpiece of a soft material, and permits the ready evaluation of the dynamic shear properties.

It is customary to describe the behavior of viscoelastic materials under linear simple harmonic deformations by a complex shear modulus having real (n') and imaginary (n'') components. The experimental measurements described in a later section for a test piece of vulcanized butyl rubber are expressed in terms of the real component n' and the damping factor d, or ratio n''/n'. The latter quantity is alternatively described as the tangent of the angle δ of mechanical loss.

EXPERIMENTAL ARRANGEMENT

The apparatus is shown diagrammatically in Figure 1. The testpiece consists of a pair of rubber cylinders R bonded on their plane faces to metal endpieces. The rubber cylinders are disposed on a common axis, with the inner metal endpieces fastened rigidly together to form the composite testpiece. The outer metal endpieces are secured in double ball races so that the testpiece may rotate freely about its axis, the rotation being imposed by a belt drive from a variable-speed motor. The central endpieces are surrounded by a ball race to the outer casing of which weights are applied, thus producing a vertical movement at right-angles to the axis of rotation. The two rubber cylinders are thus subjected to a simple shear deformation, the direction of which is continuously rotated.

* Reprinted from the *British Journal of Applied Physics*, vol. 11, pages 165–167, April 1960.

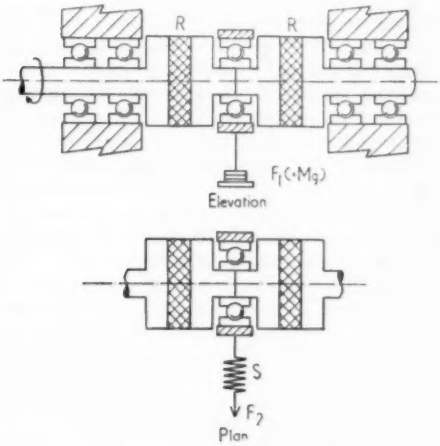

FIG. 1.—Experimental arrangement.

The central ball-race assembly moves spontaneously out of alignment, by a horizontal displacement perpendicular to the axis of rotation. This displacement is caused by energy dissipation in the rubber cylinders. By means of a calibrated helical spring S the magnitude of the horizontal force F_2 necessary to restore the central assembly to its original position in the horizontal plane may be determined. This constitutes one of the experimentally-observed quantities; the other is the magnitude of the vertical deflexion ϵ of the central assembly under the imposed vertical force F_1.

DETERMINATION OF n' AND d

The rotating shear displacement to which the rubber cylinders are subjected may be resolved into two linear, mutually perpendicular, simple harmonic motions:

$$x = \epsilon \sin pt$$
$$y = \epsilon \sin (pt + \tfrac{1}{2}\pi)$$

where p is the rotation velocity. The corresponding sinusoidally-varying forces are readily calculated. They are found to constitute a rotating force which leads the rotating displacement ϵ by an angle δ (equal to $\tan^{-1}d$), and is of magnitude $A(n'^2 + n''^2)^{1/2}\epsilon$, where A is the geometrical constant for the testpiece. (A is given by $2\pi r^2/h$ for two cylinders of radius r and thickness h.)

The force component F_1 in phase with the displacement is, therefore:

$$F_1 = An'\epsilon$$

and the component F_2, perpendicular to it, is given by:

$$F_2 = dF_1$$

The dynamic shear properties n' and d are therefore simple functions of the experimentally-observed quantities.

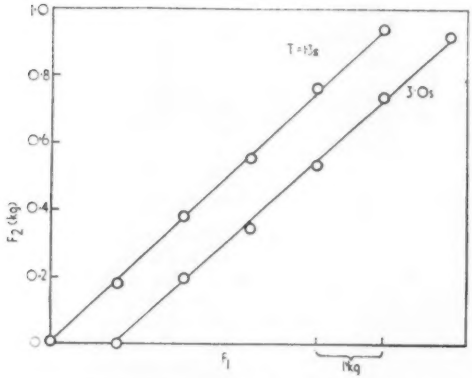

FIG. 2.—Experimental relations between F_2 and F_1 at two periods of revolution, 1.3 and 3.0 seconds.

EXPERIMENTAL RESULTS

In Figure 2, measured values of the horizontal force F_2 necessary to restore the central assembly to its initial position horizontally are plotted against the corresponding values of the imposed vertical force F_1 for two rates of rotation, for testpieces of a butyl rubber vulcanizate. The rubber cylinders were 1.27 cm in radius and 0.635 cm thick. The mix-formulation and vulcanization conditions are described in the Appendix. The periods of revolution were 1.3 and 3.0 seconds.

Linear relations are seen to apply, within the experimental error, and from the slopes, values of the damping factor d of 0.186 and 0.179 respectively are obtained. Linear relations were also obtained between the vertical deflection ϵ and the applied vertical load F_1. From the slopes, values of the shear modulus n' were calculated at a number of different periods of revolution. The values obtained, corrected for the small bending contribution (about 3%) with testpieces of the present dimensions[5], are given in Table I.

Measurements were also made of the decay of torsional oscillations in the same testpieces. A large inertia beam was attached to one metal endpiece at right-angles to the axis of the testpiece and set swinging, the other metal endpiece being rigidly clamped. The oscillations were observed by means of a lamp and scale, and were found to decay logarithmically, as is shown in Figure 3, where a representative plot of the double amplitude of swing against

TABLE I

DYNAMIC SHEAR PROPERTIES FROM (*a*) ROTARY MACHINE AND (*b*) FREE TORSIONAL OSCILLATIONS

Period, T (s)	*a*		*b*	
	n' (kg/cm²)	d	n' (kg/cm²)	d
0.55	3.65	—	—	—
1.30	—	0.186	3.43	0.184
1.72	3.26	—	3.38	0.174
3.00	—	0.179	—	—
3.40	3.14	—	3.52	0.170

the number of swings is portrayed. Values of the damping factor d were calculated from the slope of similar linear relations for a number of values of the period of oscillation, varied by suitably adjusting the inertia of the swinging beam. The values obtained are given in the table, together with the corresponding values of the shear modulus n', calculated from the measured period of vibration, the moment of inertia and the testpiece dimensions.

The free-vibration measurements are seen to be in good agreement with the rotary-machine observations, over the restricted range of frequencies practicable with the former system. The values obtained for d are closely similar to those obtained by means of the rotary machine, at corresponding periods of revolution. The values of n' are similar to, but slightly larger than, the corresponding rotary-machine determinations. This may be due to inaccuracy in determining the testpiece dimensions—particularly the radius, which enters the calculation of torsional stiffness to the fourth power—or to slight yielding of the ball-race grips, which would contribute to the observed deflections with the rotary machine.

DISCUSSION

It has been commonly assumed that the energy dissipated in one deformation cycle is a constant, or substantially constant, fraction of the maximum energy stored in the material during the deformation. This conception leads to anomalies when the deformation cycle does not contain the origin, that is, when a *deformed* rubber is subjected to a deformation cycle about its deformed state[6]. Greenwood and Tabor[1], in considering energy dissipation during complex deformation cycles, have suggested that energy may be dissipated even when the elastically-stored energy is held constant.

The rotary machine described imposes a simple shear of constant amount, but the direction of which is continuously rotated. The elastically stored energy is, of course, unchanged on rotation. The existence of the force F_2, and the energy dissipation it reflects, therefore constitutes an effective substantiation of Greenwood and Tabor's hypothesis.

Other deformation cycles can be envisaged which have a maximum stored energy equal to the (constant) value in the present one. The amount of

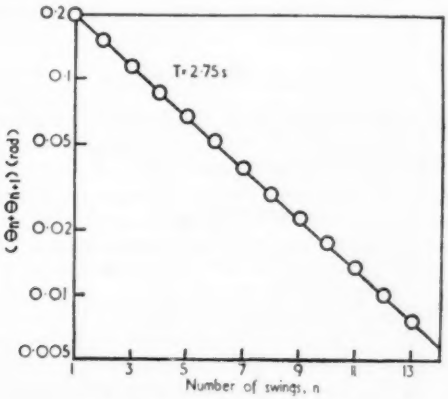

FIG. 3.—Decay of torsional oscillations.

energy dissipated per cycle may well differ, however. For example, in a simple shear oscillation, the energy dissipated per cycle is $\pi A n'' \epsilon^2$, whereas a rotating shear of the same amount gives rise to an out-of-phase force F_2 (equal to $A n'' \epsilon$) acting over a distance $2\pi\epsilon$ per cycle, and hence an energy dissipation per cycle of $2\pi A n'' \epsilon^2$—twice the former amount. The concept of a constant fractional energy loss is, therefore, untenable.

No attempt has been made to determine the range of conditions which may be employed with the rotary machine. It seems clear, however, that the absence of reciprocating members and substantial moving parts should permit a relatively large frequency range to be examined. The inherent simplicity of operation and the ease with which the shear properties can be derived should also make the method suitable for general application.

SUMMARY

A test machine is described for determining the dynamic shear properties of rubberlike materials. It imposes a simple shear deformation, the direction of which is continuously rotated. The observations are easily made, and enable the dynamic shear modulus and damping factor to be determined rapidly; moreover, a relatively wide frequency range seems feasible. The instrument therefore appears suitable for general application. Measurements on a soft butyl rubber vulcanizate are described and compared with observations of free torsional oscillations. Good agreement is obtained.

The testpiece is subjected to a rotating shear of constant amplitude, and hence the elastically-stored energy is held constant. The observed energy dissipation therefore confirms a hypothesis of Greenwood and Tabor[1], that dissipation may occur under such conditions, and indicates the limitations of the "hysteresis" concept that the dissipated energy is a constant fraction of the elastically-stored energy.

APPENDIX

PREPARATION OF THE TESTPIECES

The mix employed had the following composition in parts by weight: butyl rubber (Polysar Butyl 400) 100, zinc oxide 5, stearic acid 1, tetramethyl thiuram disulfide 4. Vulcanization was effected by heating for 50 min at 140° C.

ACKNOWLEDGMENTS

The author is indebted to Mr. D. J. Hill for experimental assistance. This work arises out of a program of research undertaken by the Board of the British Rubber Producers' Research Association.

REFERENCES

[1] Greenwood, J. A. and Tabor, D., *Proc. Phys. Soc. (London)* **71**, 989 (1958).
[2] Kimball, A. L., and Lovell, D. E., *Phys. Rev.* **30**, 948 (1927).
[3] Maxwell, B., *J. Polymer Sci.* **17**, 151 (1955).
[4] Maxwell, B., *J. Polymer Sci.* **20**, 551 (1956).
[5] Rivlin, R. S. and Saunders, D. W., *Trans. Inst. Rubber Ind.* **24**, 296 (1949).
[6] Davies, D. M., *Nature (London)*, **170**, 937 (1952).

ACCELERATION BY THIOUREA AND RELATED COMPOUNDS OF THE TETRAMETHYLTHIURAM DISULFIDE VULCANIZATION OF NATURAL RUBBER

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It has recently been discovered that thiourea and certain of its *N*-derivatives[1] and chemically related compounds[2], accelerate the vulcanization of natural rubber (NR) by tetramethylthiuram disulfide (TMTD)-zinc oxide combinations to such an extent that excellent vulcanizates can be produced at 100° C or lower.

A reasonable explanation of this acceleration is now offered, based on a theory of vulcanization by TMTD and related "sulfurless" curing systems currently being developed here. This theory recognizes the importance of polysulfidic intermediates (I, $m > 2$), formed during the vulcanization process, which subsequently react with the polyisoprene to yield further intermediates (II) which finally react to yield sulfurated crosslinks.

The process is broadly schematized as follows:

$$(m-1)\,\mathrm{XSSX} \xrightarrow{\mathrm{ZnO}} \underset{(\mathrm{I})}{\mathrm{X{-}S_m{-}X}} + \frac{m-2}{2}\,\{(\mathrm{XO})_2\mathrm{Zn} + (\mathrm{XS})_2\mathrm{Zn}\} \quad (1)$$

$$\mathrm{RH} + \mathrm{X{-}S_m{-}X} \xrightarrow{\mathrm{ZnO}} \underset{(\mathrm{II})}{\mathrm{R{-}S_{m-1}{-}X}} + {}^1/_2\,\{(\mathrm{XS})_2\mathrm{Zn} + \mathrm{H_2O}\} \quad (2a)$$

$$\mathrm{RH} + \mathrm{R{-}S_{m-1}{-}X} \xrightarrow{\mathrm{ZnO}} \mathrm{R{-}S_{m-2}{-}R} + {}^1/_2\,\{(\mathrm{XS})_2\mathrm{Zn} + \mathrm{H_2O}\} \quad (2b)$$

where $\mathrm{X} = \mathrm{Me_2N{\cdot}C(:S)}{-}$; RH = rubber hydrocarbon.

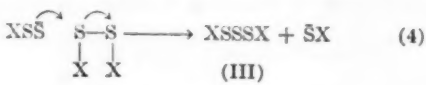
Since the crosslinking reaction (2b) follows from the products of reaction (2a) which itself requires the thiuram polysulfides (I) produced in reaction (1), it follows that any acceleration of the latter must lead also to a corresponding increase in overall vulcanization rate.

The accelerative effect of thiourea is attributed to its interaction with TMTD offering, under the prevailing basic reaction conditions, a particularly easy route for the formation of thiuram polysulfides (I). This view is perhaps more clearly understood if we inspect the mechanism of polysulfide formation in a simple TMTD-zinc oxide reaction.

Recent fundamental studies[3] on the reactivity of basic oxy-anion type nucleophils suggest that oxygen atoms of zinc oxide prefer to attack the thiocarbamyl carbon atoms of TMTD causing the following polar substitution:

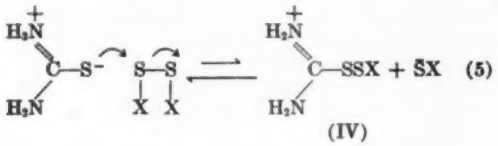
$$\ldots Zn^{++}\ldots O^{=}\ldots X\text{—}SSX \longrightarrow \ldots Zn^{++}\ldots \bar{O}X + \bar{S}SX \quad (3)$$

Reaction (3) yields a *perthioanion* ($XS\bar{S}$) which will rapidly effect the heterolysis of an S—S bond in another TMTD molecule to give the *trisulfide* (III):



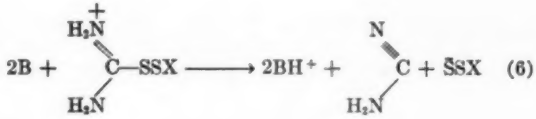
(4)

Participation of (III) in processes similar to (3) and (4) will lead to the formation of higher polysulfides (I, $m \geq 4$). It is believed that the slow steps in this propagation of thiuram polysulfides are reactions, exemplified by (3) above, in which the perthioanions are released during relatively difficult X—S bond fissions. If thiourea is added to the system it will engage in a thioanion–disulfide interchange reaction of the type:



(5)

to give a supply of (IV) which would lose a proton to a suitable base and thence decompose rapidly to a perthioanion:



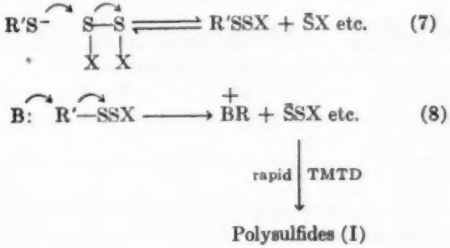
(6)

where B = base.

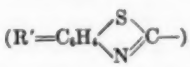
Thus the relatively easy processes (5) and (6) lead to a rapid production of perthioanion precursors of the thiuram polysulfides required in the ultimate crosslinking reactions. Our contentions as to the ease of reactions such as (6) gain support both from the early observations of Werner[4] that dithioformamidinium salts readily eliminate sulfur on treatment with aqueous sodium acetate, or on boiling with water, and from our own unpublished experiments which show that although TMTD slowly gives sulfur (*ca.* 0.7 g atoms S per g mole TMTD) on refluxing with excess sodium methoxide solution, the addition of thiourea results in an immediate liberation of sulfur.

On the basis of the present theory it is predicted that easy production of perthioanions ($X\bar{S}_x$) and hence polysulfides and a consequent acceleration of vulcanization in the NR–TMTD–ZnO system will result upon the addition

to the system of any thioanion ($R'\bar{S}$) wherein the group R′ is more susceptible than X to nucleophilic attack by bases:



Reaction (7) will be promoted by the removal of R′SSX by reaction (8) and $\bar{S}X$ as Zn $(SX)_2$. The requirement for acceleration, namely that R′ is attacked more readily than X by basic nucleophils, is fulfilled in the case of thiourea ($R' = H_2\overset{+}{N}{:}\underset{|}{C}\cdot NH_2$, easy N-proton removal) but not in its *N,N′*-tetraalkyl derivatives ($R' = Me_2\overset{+}{N}{:}\underset{|}{C}\cdot NMe_2$). The anions of thioacetic acid ($R' = \underset{|}{MeCO}$) which have a marked accelerative effect also meet the theoretical requirement. Conversely, one would expect retardation of vulcanization where the group R′ is less reactive towards basic nucleophils than is the thiocarbamyl center, X. This has recently been demonstrated by Swift[5] who has shown, first, that the rate of crosslinking in a NR–TMTD–ZnO system is decreased when mercaptobenzthiazole



is included, and second, that there is complete inhibition of cure when naphthalene-2-thiol is added to the system.

REFERENCES

[1] Fletcher, W. P. and Fogg, S. G., *Rubber J. and Intern. Plastics* **135**, 687 (1958).
[2] Philpott, M. W., unpublished.
[3] Saville, B., unpublished.
[4] Werner, E. A., *J. Chem. Soc.* 1912, 2166.
[5] Swift, P. M., unpublished.

STANDARD MATERIALS FOR RUBBER COMPOUNDING *

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When the synthetic rubber plants began operation in 1943, the Government took steps to establish a system of quality control that would assure that the rubber produced in 16 plants had essentially the same properties and could be used interchangeably by the manufacturers of rubber products. The most important characteristic for quality control was the curing behavior of the rubber. The measurement of this behavior required mixing the rubber with compounding ingredients, vulcanizing the mixed compound for several periods of time, and measuring the tensile properties of the vulcanizates.

Early interlaboratory tests led the Government to an extensive standardization program in order to achieve the necessary quality control of production. In this program, it became obvious that the compounding ingredients as well as the methods of mixing, curing, and testing required standardization. Therefore, in 1944, the Rubber Reserve Co. established standard compounding ingredients for testing synthetic rubbers. The first standards were commercial lots set aside and distributed by their suppliers, and consisted of five materials. By 1946 a total of 14 standards had been established.

The Office of Rubber Reserve soon recognized that the establishment of suitable standards was a difficult technical problem and called on the National Bureau of Standards for assistance. Finally, in 1948 this Office requested NBS to assume responsibility for these standards. Shortly thereafter, ASTM Committee D-11 appointed a special subcommittee on standard materials, the forerunner of Subcommittee 29 on Compounding Ingredients. This Subcommittee requested the establishment of about 20 standard compounding materials which included the standards required for the synthetic rubber program. The National Bureau of Standards has now available 17 of these materials, including three standard rubbers.

CRITERIA FOR STANDARDS

A satisfactory standard for rubber compounding must fulfill the following requirements: It must be uniform throughout the lot. It must not change appreciably before use. Successive lots of the standard should have the same characteristics for the intended use.

By 1947, it was evident that many of the 14 materials established as standards by the Rubber Reserve Co. did not meet these requirements and that a reappraisal of the test formulations was necessary. After an extensive study, the formulations for testing synthetic rubbers were simplified and six of the 14 materials were eliminated. Experience had shown by this time that it is very difficult to reproduce the lower commercial grades used in the rubber industry

* Reprinted from Proceedings of International Rubber Conference, Washington, D. C., November 1959, pages 232–236.

because of the many active impurities present. Therefore, many of the standards were replaced when the formulations were changed. The highest purity materials commercially available were selected for these replacements. Even the small amount of impurity in the best commercial grades has given considerable difficulty in reproducing lots of some standards.

The original standards were distributed in the customary commercial containers, which were paper bags in some instances. It was found that some materials packaged in this manner changed irreversibly during storage and could not be used after a short time. Therefore, the decision was made to package the compounding ingredients in air-tight metal containers. However, it is not expedient to package the rubbers in metal containers. They were wrapped in polyethylene and packaged in paper bags.

The stability during storage of the standards and proposed standards is being studied. Surveillance of the established standards is maintained to determine when appreciable change in their characteristics has occurred. Portions of the various materials are being stored under four different temperature conditions ranging from −20° to +40° C and periodic tests are being made. Among the NBS Standards for Rubber Compounding, the only change noted is a slight increase in Mooney viscosity of one of the styrene-butadiene rubbers, SBR-1500. On the other hand, studies made on materials proposed for use as standards indicate that many of the materials used in the rubber industry are not sufficiently stable for this purpose.

PROCUREMENT OF MATERIALS

Replacement lots are purchased on the basis of specifications for composition and performance in rubber compounds. The specifications for composition are given in Appendix A. Tests are made to determine that the material complies with these specifications, but no attempt is made to certify the actual composition. The uniformity of the lot and its suitability for a standard are judged by its performance in a standard rubber compound. In some cases several lots have to be tested before a suitable material is obtained.

Materials for the standards have been procured through the issuance of bid invitations to prospective suppliers in accordance with regular Government practices. Thus, successive lots of a standard have frequently been purchased from different suppliers. Each new supplier had to be educated on the stringent requirements enumerated above for a standard. All the suppliers have been cooperative, and have been able to furnish a satisfactory lot in most instances.

SAMPLING AND TESTING

In the case of replacement lots of compounding ingredients, several portions are selected at random from the lot prior to packaging. These portions are compared with the previous standard of the particular material to ascertain their equivalence in a standard rubber compound. Generally, four compounds are prepared from each portion and at least four compounds from the previous standard.

The uniformity of the lot is judged from a sample taken during packaging. Experience indicates that 8 to 13 portions selected at predetermined periodic intervals give a suitable sample. Each portion is tested separately in a standard rubber compound. In order to eliminate small errors attributable

to the sequence or day in which the compounds are mixed, a statistical design similar to those given in Appendix B is used.

The rubber compounds are prepared in accordance with the appropriate standard formulation and mixing procedure in ASTM Designation D 15. The compounds are mixed on a mill having rolls specially designed to maintain their surface temperature constant within 2 Celsius degrees[1]. All operations are conducted in a room conditioned at 23° ± 1° C and between 35 and 40% relative humidity.

The viscometer cure characteristics of the compound are determined at either 125° or 150° C, between 2 and 4 hours after mixing by the procedure described in ASTM Designation D 1077. In addition to the time of incipient cure (t_5), the time required for the viscosity to increase from 5 to 35 ML points above the minimum is recorded as the cure index (Δt). The parameter Δt is inversely related to the rate of cure.

Vulcanizates approximately 15 × 15 × 0.2 cm are prepared in accordance with ASTM Designation D 15 using a chromium-plated, four-cavity mold machined directly in the hot plates of the press. The press is equipped with a special temperature controller which maintains the temperature of the plates constant within 0.1 Celsius degree. This equipment produces vulcanizates that are uniform in thickness within 0.02 mm.

The following tests are made on the vulcanizates:

Test	ASTM Procedure
Strain under a fixed load	D 1456-57T
Stress at a fixed elongation	D 412-51T
Stress at failure	D 412-51T
Elongation at failure	D 412-51T
Electrical resistivity*	D 991-48T**

* Measured only on compounds containing carbon black.
** Modified as described by McKinney and Roth[2].

ANALYSIS OF RESULTS

A statistical analysis is made of the results for each property. A typical analysis is given in Appendix B for the viscometer cure results obtained with standard sample 371c of sulfur. The several analyses are examined for trends or other evidence of nonuniformity in the material. The results for most standards for rubber compounding show no evidence of heterogeneity in their effect on vulcanization characteristics. In the few instances in which some heterogeneity has been observed, either the variability is slight—i.e., not significant at the 1% level—the portion of the lot exhibiting the variability is not included in the standard sample, the lot is reblended and retested, or a new lot is prepared.

In the case of the rubbers, no attempt is made to reproduce the previous lot exactly. Instead, the most probable values and their uncertainties based on a confidence coefficient of 95% are determined and issued as a certificate with the standard. In calculating the uncertainty limits, allowance is made for intrinsic error of test and systematic effects associated with both sequence of mixing the compounds and day of mixing. In those instances where there is a slight heterogeneity in the material itself, the uncertainty limits also reflect this variability. Accordingly, the uncertainties given in the certificates for the rubbers are generally larger than would be indicated by the intrinsic error of test which is used to judge the uniformity of the lot.

PROBLEMS ENCOUNTERED IN ESTABLISHING STANDARD MATERIALS

(The NBS Standard Sample No. precedes the name of the following standard materials.)

370 Zinc oxide.—The original standard established by the Rubber Reserve Co. was made by the American process. Attempts to reproduce the material were not successful. In 1948, a high-purity zinc oxide made by the French process was chosen for the standard. No difficulty has been encountered in reproducing this material.

371 Sulfur.—A distilled product of high purity has been used for the standard. There has been no difficulty in reproducing it.

372 Stearic acid.—The original material chosen for the standard was the highest quality available at the time. It contained some impurities that had a pronounced influence on the vulcanizates of rubber compounds. It was not possible to reproduce the original standard. A distilled stearic acid of low iodine number which is equivalent in rubber to C. P. stearic acid was therefore chosen for the standard. This high quality material has been reproduced twice without difficulty.

373 Benzothiazyl disulfide.—A commercial material is used for the standard. Although the original standard has been reproduced twice, testing of many lots is required to obtain one satisfactory for the standard.

374 Tetramethylthiuram disulfide.—The standard is a commercial material that has been reproduced once after testing a number of lots.

375 Channel black.—This standard has been reproduced several times, but only after testing many lots. The several lots have had detectable differences among them, but the differences have been small enough so that they could be used for specification testing. Special blending of the lot has been necessary to attain the desired uniformity.

376 Magnesia.—The original Rubber Reserve Co. standard has been replaced with a lot having an appreciably different effect in polychloroprene. It has also been difficult to obtain a uniform lot of this material.

377–383.—The original lot established for each of these standards (see Appendix A) is still being furnished. Consequently, the problems involved in replacing them are still unknown.

385 Natural rubber.—Extensive investigations during the past 10 years were conducted to obtain a uniform lot of rubber having the desired properties. Liberian crepe produced under carefully controlled conditions was finally selected for this standard. The rubber was produced on two days. There was a slight difference between the two lots of rubber, but each lot was uniform within itself. Accordingly, the lots have been individually certified.

386 SBR-1500.—Replacement lots of styrene-butadiene rubber, type 1500, have been similar even though no attempt was made to reproduce the original exactly. There has been some difficulty in attaining the desired uniformity within the lot. The Mooney viscosity of this material has also changed slightly during storage.

387 SBR-1000.—This standard is more stable than SBR-1500, but is comparable in uniformity.

CONCLUSIONS

The standards for rubber compounding have been useful in the standardization of testing in the synthetic rubber plants. Their success in this application has resulted in their use by other rubber laboratories. However, the establishment of these standards has been and continues to be a difficult technical problem. The difficulties have been alleviated whenever a high-purity material has been obtained.

APPENDIX A

SPECIFICATIONS FOR COMPOSITIONS OF STANDARDS

370 Zinc oxide.—This standard conforms to the requirements of the American Chemical Society for reagent grade zinc oxide and has a surface area of approximately 3 square meters per gram.

371 Sulfur.—This standard is a distilled sulfur conforming to the following requirements:

Purity	99.90% minimum
Loss at 100° C	0.05% maximum
Ash	0.02% maximum
Insolubles in CS_2	0.10% maximum
Insolubles in benzene	0.10% maximum
Organic material	0.05% maximum
Acidity as H_2SO_4	0.005% maximum
Physical state	
Through 100-mesh sieve	100%
Through 200-mesh sieve	90 to 95%

372 Stearic acid.—This standard is a distilled stearic acid conforming to the following requirements:

Titer (solidification point)	65° C minimum
Iodine number	2 maximum
Loss at 105° C	0.5% maximum
Ash	0.1% maximum
Acid number	195 to 199
Mineral acid	none
Fat, unsaponifiable, and insoluble material	0.5% maximum
Physical state	Flake or powder

373 Benzothiazyl disulfide.—This standard conforms to the following requirements:

Benzothiazyl disulfide	93.0% minimum
Mercaptobenzothiazol	0.5 to 0.75%
Moisture	0.5% maximum
Ash	0.7% maximum
Mineral oil	2.0%
Zinc soap	2.0% maximum
Melting point	165° C maximum
Physical state	
Through 100-mesh sieve	99.9% minimum

374 Tetramethylthiuram disulfide.—This standard conforms to the following requirements:

Moisture	0.05% maximum
Ash	0.10% maximum
Insolubles in $CHCl_3$	0.15% maximum
Melting point	163° C minimum
Physical state	
Through 100-mesh sieve	100%

375 Channel black.—This standard conforms to the following requirements:

Loss at 100° C	2.00% maximum
Ash at 550°C	0.15% maximum
Physical state	
Retained on 325-mesh sieve	0.10% maximum
Retained on 30-mesh sieve	0.001% maximum

376 Light magnesia.—This standard conforms to the following requirements:

Magnesium oxide	91.0% minimum
Loss on ignition	7.0% maximum
Calcium oxide	1.0% maximum
Water solubles	1.0% maximum
Acid insolubles	0.4% maximum
Fe_2O_3 and Al_2O_3	0.1% maximum
Manganese	0.004% maximum
Density	10 lb/cu ft maximum
Physical state	
Retained on 325-mesh sieve	0.1% maximum

377 Phenyl-beta-naphthylamine.—This standard is distilled phenyl-beta-naphthylamine conforming to the following requirements:

Phenyl-beta-naphthylamine	99.25% minimum
Loss at 105° C	0.25% maximum
Ash	0.25% maximum
Beta-naphthol	0.10% maximum
Benzene insolubles	0.10% maximum
Melting point	107° C minimum
Physical state	
Retained on 100-mesh sieve	0.10% maximum

378 Oil furnace black.—This standard conforms to the following requirements:

Loss at 100° C	1.0% maximum
Ash at 550° C	0.5% maximum
Physical state	
Retained on 325-mesh sieve	0.1% maximum
Retained on 30-mesh sieve	0.005% maximum

379–382. 379 Conducting black, 380 Calcium carbonate, 381 Calcium silicate, and 382 Gas furnace black.—These standards are commercial materials supplied through ASTM Committee D-11 so that no requirements for composition have been established.

383 Mercaptobenzothiazole.—This standard conforms to the following requirements:

Mercaptobenzothiazole	99.0% minimum
Moisture	0.3% maximum
Ash	0.3% maximum
Melting point	179° C minimum
Physical state	
Retained on 100-mesh sieve	0.1% maximum

385 Natural Rubber.—This standard conforms to the following requirements:

Rubber hydrocarbon	92.0% minimum
Volatile matter	0.5% maximum
Ash	0.5% maximum
Dirt (retained on 325-mesh sieve)	0.05% maximum
Copper	0.0004% maximum
Manganese	0.0005% maximum

386 SBR-1500.—This standard conforms to the following requirements:

Volatile matter	0.75% maximum
Ash	1.50% maximum
Rosin acid	5.00 to 7.25%
Soap	0.50% maximum
Stabilizer	1.00 to 1.75%
Bound styrene	22.5 to 24.5%

387 SBR-1000.—This standard conforms to the following requirements:

Volatile matter	0.50% maximum
Ash	1.50% maximum
Fatty acid	4.00 to 6.25%
Soap	0.75% maximum
Stabilizer	1.00 to 1.75%
Bound styrene	22.5 to 24.5%

APPENDIX B

DESIGN FOR VULCANIZATION TESTS

The design of test selected for determining the uniformity of a standard for rubber compounding with respect to the vulcanization characteristics of the rubber compound depends on the number of portions comprising the sample, which usually is between 8 and 13. Further, the design must accommodate tests in groups of four because four compounds are vulcanized simultaneously. Also, experience indicates that four compounds should be prepared from each portion in the sample in order to attain the desired precision for evaluating the standard. The following designs fulfill these requirements:

Sample size	Ref. Design*
8	(3) page 142, design Sr 7
9	(3) page 186, design R 8
10	(3) page 232, design T 12
11	None available
12	(3) page 188, design R 15
13	(4) page 145, table 13.6

These publications give instructions for analyzing these designs.

For illustration, the following design was used recently to evaluate NBS Standard Sample 371c of sulfur:

Order of mixing	Day of mixing											
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*k*	*m*	*n*
A	4	1	9	8	12	10	11	2	5	7	6	3
B	5	3	10	12	1	11	4	7	8	6	9	2
C	1	6	5	2	7	8	12	10	3	11	4	9
D	2	10	12	6	9	1	3	4	7	5	8	11

The numerals correspond to the twelve portions in the order in which they were taken from the lot. The following table lists the times in minutes for incipient cure, t_5, measured in the Mooney viscometer at 150° C.

Portion	A	B	C	D	Observed mean
1	8.26b	8.78e	8.46a	8.43f	8.482
2	8.45h	8.57n	8.55d	8.49a	8.515
3	8.60n	8.39b	8.43i	8.31g	8.432
4	8.45a	8.49g	8.48m	8.46h	8.470
5	8.28i	8.45a	8.70e	8.50k	8.482
6	8.58m	8.58k	8.47b	8.57d	8.550
7	8.58k	8.52h	8.56e	8.47i	8.532
8	8.25d	8.36i	8.38f	8.63m	8.405
9	8.23c	8.43m	8.57n	8.56e	8.448
10	8.32f	8.40c	8.69h	8.48b	8.472
11	8.52g	8.52f	8.54k	8.58n	8.540
12	8.33e	8.56d	8.40g	8.51c	8.450
					8.482

An analysis of variance following the procedure given in Table 1.0 (Ref. 3, page 5) gives the following results:

Source of variation	Degrees of freedom	Sum of squares	Mean square
Portions	11	0.0936	0.0085
Days	11	0.2000	0.0182
Order	3	0.0987	0.0329
Error	22	0.2663	0.0121

The mean square for portions is less than that for error indicating no detectable difference among portions. The mean square for error corresponds to a standard deviation for a single measurement of 0.11 minute. The variability arising from day and order is small so that this design of test offers no advantage over a completely random design in this instance. Frequently, there is an appreciable variability arising from day and order. In such cases, the above designs have advantages in detecting heterogeneity in the lot.

The following tabulation lists the mean squares for portions and error calculated from the results for the various tests, and the minimum and maximum means for the 12 portions corrected for day effects.

Tests	Mean square		Portions	
	Portion	Error	Min.	Max.
Incipient cure, t_5, min	0.0085	0.0121	8.37	8.55
Cure index, $t_{35}-t_5$, min	0.0052	0.0040	3.08	3.23
Strain at 400 psi, %				
15-min cure	41	67	300	309
30-min cure	3.25	2.47	170	172
60-min cure	2.48*	0.80	141	143
Stress at 300%, psi				
15-min cure	583	363	467	516
30-min cure	237	675	1169	1200
60-min cure	243	553	1557	1585
Stress at failure, psi				
30-min cure	6938	27218	4189	4333
Elongation at failure, %				
30-min cure	63	188	623	640
Resistivity, megohm-cm				
60-min cure	52	54	59	71

* This value is significantly greater than that for error. However, the error mean square usually obtained for this compound is above 2. Further, there is no evidence of any trend in the portions. In view of no other evidence of heterogeneity, it is concluded that the lot of sulfur is uniform.

REFERENCES

[1] Roth, F. L., Decker, G. E. and Stiehler, R. D., "Temperature Control During Mixing of Rubber Compounds", *Rubber World* **132**, 482 (1955); RUBBER CHEM. & TECHNOL. **28**, 1157 (1955).
[2] McKinney, J. E. and Roth, F. L., *Ind. Eng. Chem.* **44**, 159 (1952).
[3] Bose, R. C., Clatworthy, W. H. and Shrikhande, S. S., *N. Carolina Exptl. Sta. Tech. Bull.* **107**, August 1954.
[4] Brownlee, K. A., "Industrial Experimentation", Chemical Publ. Co., Brooklyn, N. Y., 1949.

VOLATILIZATION OF PHENYL-2-NAPHTHYLAMINE FROM RUBBER *

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Some of the ingredients present in polymers may evaporate (or volatilize) under vacuum or by the action of heat. Volatilization of ingredients occurs during treatment of polymers at high temperatures, during curing of rubber goods in pans, during accelerated thermal aging of polymeric materials in thermostats, and from certain articles in use. The loss of ingredients increases with the free volume in which the polymer is present. Softeners, plasticizers, antioxidants, and free sulfur readily volatilize from various rubbers.

Volatilization of the most important ingredients present in polymeric materials has an adverse effect on their main physicochemical and mechanical properties, and their performance deteriorates accordingly. Moreover, volatilization of ingredients is accompanied by their migration from one polymer material into another when different materials are aged together in thermostats, and this leads to erroneous estimates of their heat stability[1].

Much information on the subject of migration has been published by ISO[2]. Until recently volatilization of various additives from polymers has not been studied widely enough from the scientific aspect. The only process to be studied in any detail was volatilization of plasticizers from plastics under atmospheric pressure and under vacuum[3].

The present investigation was undertaken in order to establish the empirical relationships which characterize the behavior of ingredients in raw and cured rubbers under various conditions, and for a theoretical examination of the problem.

In these investigations the volatilization of antioxidant from a rubber slab heated in a stream of gas was studied. The antioxidant was phenyl-2-naphthylamine.

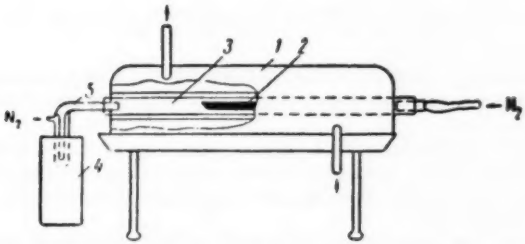

Fig. 1.—Apparatus for studying the kinetics of ingredient volatilization from raw and cured rubbers in a current of gas: *1*) Horizontal tubular furnace; *2*) slab of raw or cured rubber; *3*) glass tube, d = 18 mm; *4*) Dewar flask; *5*) detachable trap.

* Translated from *Kolloidnyi Zhurnal*, Vol. 22, pp. 2–8, January–February, 1960 and reprinted from the *Colloid Journal* **22**, pages 1 to 7 1960.

The investigation procedure was as follows: Sodium butadiene rubber (SKB without antioxidant) was mixed on a micro roll mill with phenyl-2-naphthylamine; plates of the required thickness were molded from the resultant mix at 70°. The antioxidant was volatilized from rubber slabs of standard surface area (150 × 10 mm) in glass tubes 18 mm in diameter; the rubber specimens were placed on glass supports. The tube was placed in a horizontal tubular surface heated by silicone fluid circulated from a Wobser thermostat (Figure 1). A current of nitrogen passing through the tube removed the antioxidant vapor from the heated part of the tube into an attached trap immersed

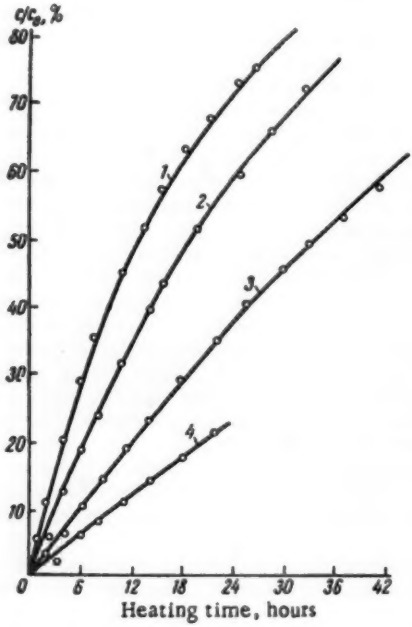

FIG. 2.—Kinetics of volatilization of phenyl-2-naphthylamine from SKB at various temperatures: *1*) 150°; *2*) 140°; *3*) 130°; *4*) 120°.

in freezing mixture. The antioxidant condensed in the trap and was estimated quantitatively by a colorimetric method. Volatilization was studied at temperatures above 100°.

Volatilization of the ingredient may depend both on the characteristics of the test specimen (plate thickness, initial concentration of ingredient in the specimen, etc.) and on the experimental conditions (temperature, velocity of the nitrogen stream, etc.).

Accordingly, the investigation consisted of determinations of the process kinetics in relation to the above-named factors.

Figure 2 represents the kinetics of volatilization of phenyl-2-naphthylamine (initial concentration 2%) from a slab of SKB 1.35 mm thick in a current of nitrogen flowing at 140 ml/minute at various temperatures. The curves are

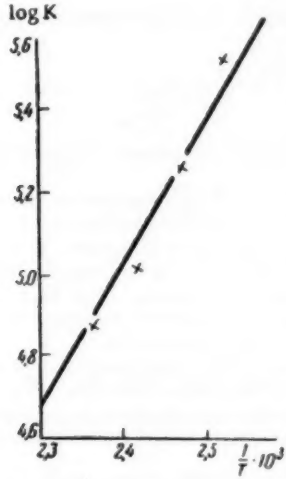

FIG. 3.—Effect of temperature on the rate constant K of volatilization of phenyl-2-naphthylamine from SKB.

satisfactorily represented by the expression:

$$\frac{c}{c_0} = 1 - e^{-Kt} \tag{1}$$

where c is the amount of ingredient lost at time t, as per cent by weight of rubber; c_0 is the initial content of ingredient in the rubber, in % by weight; K is a constant.

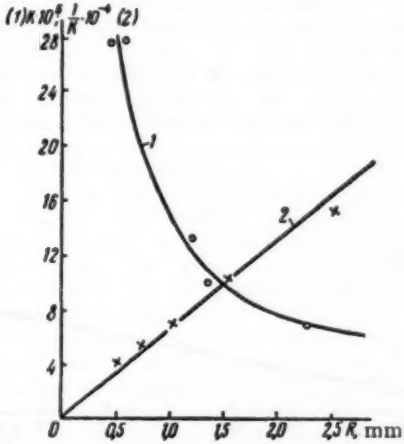

FIG. 4.—Effect of slab thickness on the rate constant of volatilization of phenyl-2-naphthylamine at 140° and nitrogen velocity 140 ml/min.

Differentiation of Equation (1) with respect to t gives an expression for the rate of volatilization:

$$v = \frac{dc}{dt} = K(c_0 - c) = Kc_1 \tag{2}$$

where c_1 is the amount of ingredient present in the rubber at time t, as per cent by weight of rubber.

This expression corresponds to the equation for a reaction of the first order, and accordingly the constant K is the volatilization rate constant. The values of K for different temperatures were calculated by rectification of the corresponding kinetic curves in $\ln (1 - c/c_0) - t$ coordinates and calculation of the slopes of the straight lines so obtained. The effect of temperature on the volatilization rate constant is represented in Figure 3. The activation energy of the process was found to be 14 kcal/mole.

The relationship between the volatilization rate and slab thickness was studied for specimens of R from 0.45 to 2.65 mm. The results show (Figure 3, Curve 1) that the volatilization rate drops sharply with increasing plate thickness. The constant K is inversely proportional to the slab thickness (Figure 4, Curve 2).

For studies of the influence of the initial antioxidant concentration on its rate of volatilization from rubber, slabs in which the antioxidant concentration was varied from 0.3 to 1.5% were used. The relationship between the volatilization rate constant and the initial concentration of the ingredient in this concentration range is linear (Figure 5) and is represented by the equation

$$K = K'(1 + ac_0) \tag{3}$$

where a is a constant calculated from the experimental data (the equation is valid at $c > 0$).

Polymers and rubber products in use are often surrounded by moving air. We therefore studied volatilization of phenyl-2-naphthylamine from rubber in a current of nitrogen the flow rate of which was varied from 15 to 1000 ml/minute. The results are plotted in Figure 6. It is clear from Figure 6 (Curve 1) that the rate of volatilization increases with the flow rate of the nitrogen stream (W). Curve 1 is rectified in $W/K - W$ coordinates (Curve 2), and the relationship between K and the gas flow rate can be represented by the following function:

$$K = K''\left(\frac{W}{b + W}\right) \tag{4}$$

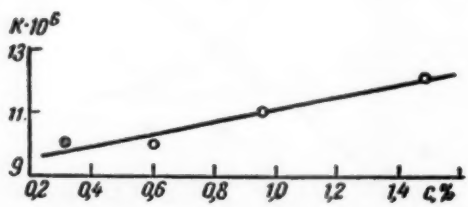

FIG. 5.—Effect of initial concentration of phenyl-2-naphthylamine on the volatilization rate constant at 140° and nitrogen flow rate 140 ml/min.

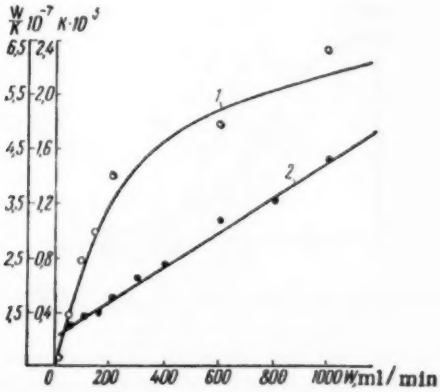

FIG. 6.—Effect of nitrogen flow rate at 140° on the rate constant of volatilization of phenyl-2-naphthylamine.

where b is a constant determined experimentally.

On the basis of these experimental results, we can write the following expression for the volatilization rate constant:

$$K = K_0 e^{-E/RT} \left(\frac{W}{b + W} \right) (1 + ac_0) \cdot \frac{1}{R} \tag{5}$$

where E is the activation energy of the volatilization process in kcal/mole; K is a constant which depends on the nature of the polymer and ingredient.

Equations (1) and (5) can be used for finding the amounts of ingredients volatilized from different polymers under various conditions. The values of K_0 and E for a given system are found experimentally.

It is likely that these relationships are of the same character in volatilization of other ingredients.

As already noted, the question of volatilization of ingredients from cured rubbers, which differ from polymers by the presence of a spatial network, is of great practical interest. It was accordingly necessary to study how the volatilization process changes in the transition from raw rubber to vulcanizates with different densities of the spatial network.

The vulcanizates were prepared by irradiation of rubber slabs 1 mm thick in TRTs-ZA x-ray tubes for radiochemical investigations, developed by the Institute of Physical Chemistry of the Academy of Sciences, USSR, under nominal tube conditions of 80 kv and 200 ma. The density of the vulcanization network was characterized by the equilibrium modulus (E_∞), the value of which varied from 13 to 38 kg/cm^2.

Figure 7 shows that the volatilization rate of phenyl-2-naphthylamine falls sharply with increasing density of the spatial network. It follows that ingredients must volatilize much more slowly from cured rubbers than from uncured polymers.

It was also of interest to find how volatilization is influenced by fillers, which are essential ingredients of most rubber stocks.

Figure 8 shows kinetic curves for volatilization of phenyl-2-naphthylamine

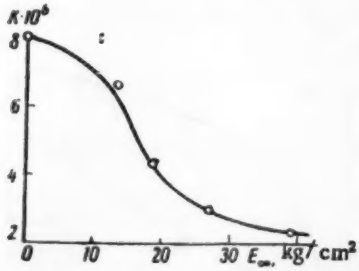

FIG. 7.—Variations of the volatilization rate constant with the equilibrium modulus of the vulcanizate at 130° and nitrogen flow rate 160 ml/min.

from rubber without filler and from rubber containing channel black and chalk in the proportions of 60 weight parts per 100 weight parts of rubber.

The results show that both fillers reduce the volatilization rate of phenyl-2-naphthylamine appreciably, and channel black has a greater decreasing effect than chalk.

The effect of the nature of the polymer on volatilization kinetics was then studied. The experiments showed that the volatilization rate of phenyl-2-naphthylamine decreases in the following series of polymers: polyethylene > fluoroprene rubber > SKB > SKS-30 > SKN-26 > Nairit (Figure 9).

This series coincides almost completely with the series of polymers in order of solubility and heat of solution of phenyl-2-naphthylamine in them[4, 5]. Accordingly, the differences in the rates of volatilization of the antioxidant from different polymers may be attributed to mutual influence of the solute and polymer molecules, leading to different values of the vapor pressure of phenyl-2-

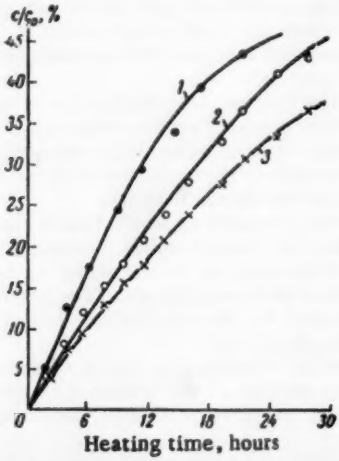

FIG. 8.—Kinetics of volatilization of phenyl-2-naphthylamine from SKB at 150° and nitrogen flow rate 160 ml/min: *1*) rubber without filler; *2*) rubber with 60 wt parts of chalk; *3*) rubber with 60 wt parts of channel black.

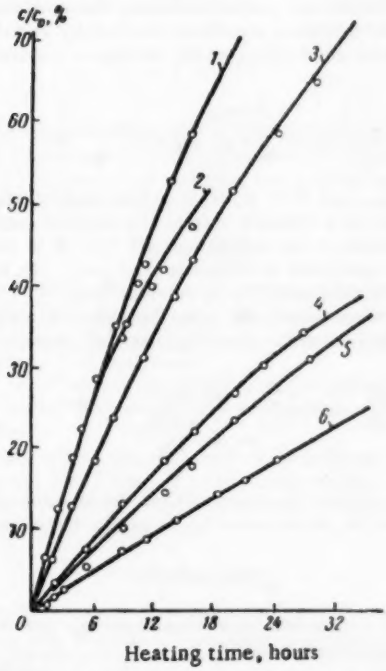

FIG. 9.—Kinetics of volatilization of phenyl-2-naphthylamine from different polymers at 140° and nitrogen flow rate 140 ml/min: *1*) Polyethylene; *2*) SKF-32; *3*) SKB; *4*) SKS-30; *5*) SKN-26; *6*) Nairit.

naphthylamine over the polymers. Variations of vapor pressure influence the volatilization rate.

In the light of the modern theory of evaporation of liquids[6] and of the mechanism of diffusion of substances of low molecular weight in polymers[4, 7] it may be postulated that in general the volatilization of ingredients from polymers proceeds in two stages: 1) Diffusion of the substance through the slab of polymer, and 2) removal of molecules of the substance from the slab surface.

The first stage of volatilization conforms to Fick's law

$$\frac{\partial c(x, t)}{dt} = D \frac{\partial^2 c(x, t)}{\partial x^2} \tag{6}$$

where $\partial^2 c/\partial x^2$ is the derivative of the concentration gradient; D is the coefficient of diffusion.

In the second stage the rate of removal of the substance from the surface must be proportional to the surface concentration of the substance (c_s), or

$$\frac{dQ}{dt} = mc_s \tag{7}$$

where m is a constant.

By analogy of diffusion and heat conduction, the volatilization process may be represented by the following equation, derived by suitable transformation of the equation for heat conduction under analogous conditions[8]:

$$\frac{c_1(x, t)}{c_0} = \sum_{n=1}^{\infty} \frac{2 \sin \mu_n}{\mu_n + \sin \mu_n \cdot \cos \mu_n} \cdot \cos \mu_n \frac{x}{R} \cdot e^{-\mu_n^2 Dt/R^2} \tag{8}$$

where $\mu_n = HR \cot \mu_n$, and $H = m/D$; c_1 is the concentration (wt. %) of the substance in the slab at a distance x from the covered surface at time t; c_0 is the initial concentration of the substance (wt %); R is the thickness of the slab (cm); D is the coefficient of diffusion (cm²/sec). In Equation (8), when x is equal to the slab thickness (R), c_1 is equal to c_s.

Substituting the expression for c_s into Equation (8) and transforming, we have the following expression for the volatilization kinetics

$$\frac{dQ}{dt} = mc_0 \sum_{n=1}^{\infty} \frac{\sin 2\mu_n}{\mu_n + \dfrac{\sin 2\mu_n}{2}} \cdot e^{-\mu_n^2 (Dt/R^2)} \tag{9}$$

At the same time, it may be assumed that the amount of substance volatilized (per unit surface) is proportional to its total content in the slab, i.e.,

$$dQ = Rdc \tag{10}$$

Substituting this expression into Equation (9), we have the following expression for the volatilization rate:

$$\frac{d(c/c_0)}{dt} = \frac{m}{R} \times \sum_{n=1}^{\infty} \frac{\sin 2\mu_n}{\mu_n + \dfrac{\sin 2\mu_n}{2}} \cdot e^{-\mu_n^2 (Dt/R^2)} \tag{11}$$

It has been shown that in the case of heat transfer the mechanism of the process is determined by the value of HR. Thus, when $HR < 0.1$ the rate is limited by the rate of heat loss to the surroundings, which in the case of volatilization corresponds to the rate of removal of the substance from the slab surface. When $100 > HR > 0.1$, the volatilization rate is determined both by the rate of heat loss to the surroundings and by the rate of diffusion through the slab.

By substitution of our experimental data into Equation (11) the value of HR can be determined. It was found that in volatilization of phenyl-2-naphthylamine from rubber at temperatures above 100° $HR < 0.1$. Hence, it may be concluded that the kinetics of the process is determined by the rate of removal of the ingredient from the slab surface. Diffusion of the substance in the polymer is not a determining factor under these conditions. At such low values of $HR \sin \mu_n$ can be replaced by μ_n, and μ_n^2 by HR. Moreover, in this case the first term in the sum of Equation (11) is sufficient.

With these simplifications we have the following expression for the volatilization rate:

$$\frac{d(c/c_0)}{dt} = \frac{m}{R} e^{-(m/R)t} \tag{12}$$

In the integral form, Equation (12) becomes:

$$\frac{c}{c_0} = 1 - e^{-(m/R)t} \tag{13}$$

It is easy to see that this equation is analogous to the empirical function given above, which represents the kinetic curves for volatilization of ingredients [Equation (1)]. This agreement confirms the validity of the foregoing concepts of the mechanism of volatilization.

SUMMARY

1. The rate of volatilization of phenyl-2-naphthylamine from a rubber slab depends on the flow rate of gas over the slab, the slab thickness, and the initial concentration of the ingredient. The activation energy of the volatilization process is 14.0 kcal/mole.

2. The rate of volatilization of phenyl-2-naphthylamine diminishes in the following polymer series: polyethylene > fluoroprene rubber > SKB > SKS-30 > SKN-26 > Nairit.

3. The volatilization rate drops sharply with increase of the density of the vulcanization network, and decreases in presence of fillers.

4. The mechanism postulated for volatilization of ingredients from polymers is confirmed by theoretical calculations.

REFERENCES

[1] Juve, A. E. and Shearer, R., *India Rubber World* **128**, 5, 623 (1953); Thomson, R. N. and Grace, N. S., *India Rubber World* **128**, 216 (1953); Schonlau, W. J., *India Rubber J.* **127**, 7, 4 (1954).

[2] Fackler, M. B. and Rugg, J. S., International Organization for Standardization, ISO/TK, Documents No. 107, 98, 102. See also Fackler and Rugg, RUBBER CHEM. & TECHNOL. **25**, 331 (1952); *Anal. Chem.* **23**, 1646 (1951).

[3] Zöhrer, K. and Merz, A., *Kunststoffe* **45**, 1 (1955); Quackenbos, H. M., *Ind. Eng. Chem.* **46**, 6, 1935 (1954); Boyer, R. F., *J. Appl. Phys.* **20**, 540 (1949); Morris, R. E. and Barrett, A. E., *Rubber Age* **75**, 76 (1954); Thinius, K., *J. prakt. Chem.* **3**, 50 (1956).

[4] Kuzminskii, A. S., Reitlinger, S. A. and Shemastina, E. V., in the book: "Aging and Fatigue of Raw and Cured Rubber and Increase of Their Endurance" [In Russian] (1955), p. 130.

[5] Reitlinger, S. A. and Kuzminskii, A. S., *Zhur. Priklad. Khim.* **27**, 2, 214 (1954).

[6] Sklyarenko, S. I. and Baranaev, M. K., *Zhur. Fiz. Khim.* **8**, 1, 51 (1936); Sklyarenko, S. I. and Baranaev, M. K., *Zhur. Fiz. Khim.* **7**, 549 (1936); Baranaev, M. K., *Zhur. Fiz. Khim.* **13**, 1635 (1939).

[7] Barrer, R. Diffusion in and Through Solids [Russian Translation] (IL, Moscow, 1948); Kuzminskii, A. S., Reitlinger, S. A. and Shemastina, E. V., *Kolloid Zhur.* **18**, 707 (1956); Kemp, A. R., Malm, F. S., Winspear, G. G. and Stiratelli, B., *Ind. Eng Chem.* **32**, 1075 (1940).

[8] Lykov, A. V., Heat Conduction in Nonsteady Process [In Russian] (Gosenergoizdat, 1948), p. 42.

ANTIOXIDANT EFFICIENCY OF p-PHENYLENE-DIAMINES IN NATURAL RUBBER VULCANIZATES *

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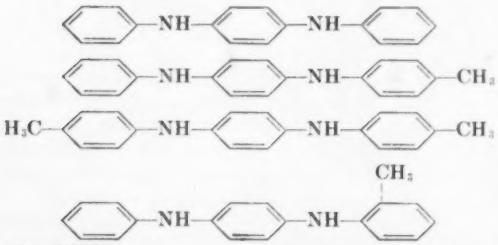
INTRODUCTION

In recent years *p*-phenylenediamines have gained considerable importance as antioxidants and antiozonants for elastomers. Three types are widely used: N,N′-di-*sec*-alkyl-, N-*sec*-alkyl-N′-aryl-, and N,N′-diaryl-*p*-phenylenediamines. The present work is concerned with the antioxidant efficiency of these three types of *p*-phenylenediamines during the oxidation of natural rubber vulcanizates. As the protection of a rubber product, particularly against ozone, can be assured only if the additive is not used up rapidly, the consumption of the inhibitor during aging is an important consideration. Therefore, special emphasis has been placed on the consumption of these diamines during oxidation. The effect of various experimental conditions on the rate of diamine consumption was studied, oxygen absorption being used to follow the oxidation.

EXPERIMENTAL

Suitable samples of about 0.6 mm thickness were prepared from the formulations given in Table I. After vulcanization, the samples were extracted with acetone and then chloroform (6 days at room temperature for each) to remove unreacted sulfur and accelerator, soluble reaction products of the accelerator, and natural antioxidants. The *p*-phenylenediamines were introduced into the vulcanizates by means of a swelling technique. The vulcanizates were swollen in a benzene-acetone mixture (4:1 volume) containing the diamine, the amount having been previously calculated from swelling measurements. After 72 hours at room temperature in this solution, the samples were removed, dried *in vacuo*, and stored under nitrogen. The final concentration of the diamine was determined by potentiometric titration as described below.

The following *p*-phenylenediamines were selected for study:



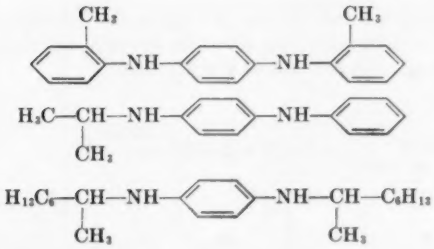
N,N′-diphenyl-*p*-phenylenediamine

N-phenyl-N′-*p*-tolyl-*p*-phenylenediamine

N,N′-di-*p*-tolyl-*p*-phenylenediamine

N-phenyl-N′-*o*-tolyl-*p*-phenylenediamine

* This paper was presented at the Meeting of the Division of Rubber Chemistry of the American Chemical Society in Louisville, Kentucky, April 19–21, 1961. Contribution No. 268 from the Research Laboratory of the Goodyear Tire & Rubber Company.

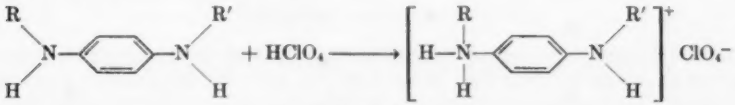


N,N′-bis-*o*-tolyl-*p*-phenylenediamine

N-isopropyl-N′-phenyl-*p*-phenylenediamine

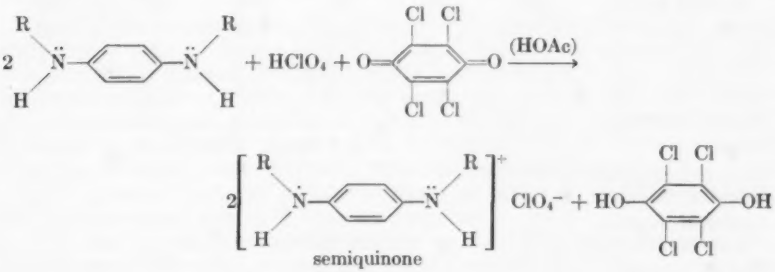
N,N′-bis(1-methylheptyl)-*p*-phenylenediamine

Oxidation was carried out in pure oxygen at 740 mm pressure in a range of 80° to 120° C. A volumetric oxygen absorption method was used to determine quantitatively the amount of oxygen absorbed[1]. To study the kinetics of the consumption of the diamines, identical samples were oxidized under uniform conditions for various times. After oxidation, the samples were extracted with acetone at room temperature for six days, the solvent being changed every two days. To determine the unconsumed *p*-phenylenediamine, several methods were used[2]. Dialkyl- and alkyl-aryl-*p*-phenylenediamines could be determined quantitatively by direct potentiometric titration with perchloric acid in non-aqueous solvents.



R = alkyl; R′ = aryl

After the acetone from the acetone extract had been evaporated on a water bath, the residue was dissolved in a solvent, usually glacial acetic acid. Diaryl-*p*-phenylenediamines, however, were not basic enough to be titrated satisfactorily under these conditions. By the addition of an excess of chloranil to the acetic acid solution, these diamines were oxidized to the corresponding semiquinones (*p*-phenylenediaminium cations)[3]; these gave sharp endpoints when titrated with perchloric acid. The stoichiometry of this reaction can be described as follows:

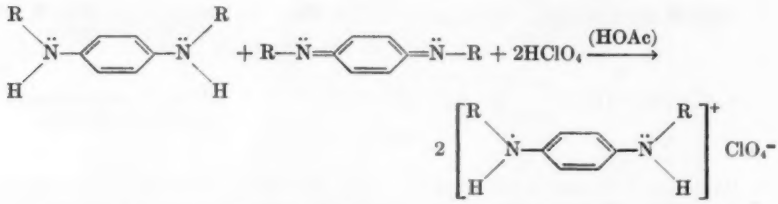


semiquinone

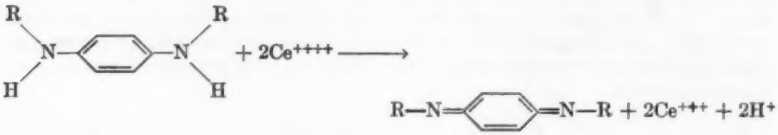
R = aryl

If the acetone extract contained the corresponding quinone diimine, this

titration furnished the sum of diamine and diimine as long as the diamine was in excess. The diimine could be determined by titration without addition of chloranil, this titration giving twice the amount of the diimine.



Oxidation of the diamines to the diimines by ceric sulfate was also used to determine quantitatively the diamine concentration, the amount of ceric sulfate consumed being determined potentiometrically.



Some of the quinone diimines were slowly oxidized by further addition of ceric sulfate as recognized by a drift of the potential after the equivalence point was reached. The oxidation of the quinone diimine, which made the detection of the endpoint uncertain, could be avoided in most cases by carrying out the oxidation in a two phase system, e.g., water-chlorobenzene.

To study the direct oxidation of some *p*-phenylenediamines in the absence of rubber, the sample tubes of the oxygen absorption apparatus were charged with three 10 ml beakers, each containing about 150 mg of the diamine. The

TABLE I

COMPOUNDING AND CURING

Compound	(1)	(2)	(3)	(4)	(5)	(6)
Natural rubber (smoked sheet)	100	100	100	100	100	100
HAF black				50		50
Zinc oxide		10	5	5	5	5
Stearic acid			3	3	3	3
Dicumyl peroxide	1.40					
Sulfur			1.50	1.50	3	3
Tetramethylthiuram disulfide (TMTD)		3.60				
2-(Morpholinothio)-benzothiazole			0.75	0.75		
Diphenyl guanidine (DPG)					1.20	1.20
Curing, min/° C	120 min/ 150°	180 min/ 135°	60 min/ 135°	60 min/ 135°	120 min/ 135°	120 min/ 135°

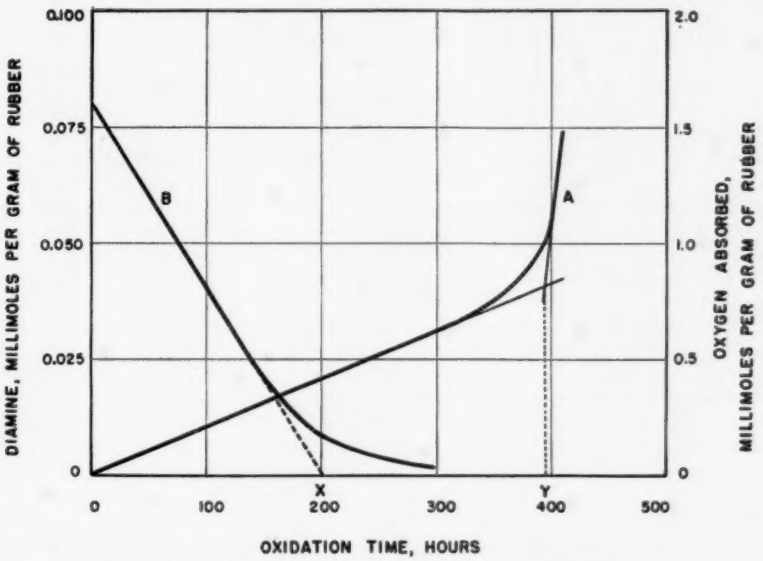


FIG. 1.—Oxygen absorption *A* and consumption of diphenyl-*p*-phenylenediamine *B* in a TMTD gum vulcanizate at 100° C. Original concentration, 2.0 phr.

oxidation was carried out at 90° C, isopropylphenyl-PD and dimethylheptyl-PD being molten at this temperature. The amount of oxygen absorbed and the amount of diamine consumed were determined in these experiments as a function of the oxidation time. Diphenyl-*p*-phenylenediamine did not react with oxygen under these experimental conditions, the amount of oxygen absorbed after 500 hours at 100° C being extremely low. The material, however, was not molten at this temperature.

RESULTS

DIARYL-*p*-PHENYLENEDIAMINES

Typical results observed in the presence of diaryl-*p*-phenylenediamines are illustrated in Figure 1 for the oxidation at 100° C of a gum vulcanizate cured with tetramethylthiuram disulfide (TMTD) and containing 2 phr of diphenyl-*p*-phenylenediamine (DPPD). In the range we investigated, the oxygen absorption curves were generally composed of two stages, a linear oxygen uptake and an autocatalytic region, Curve *A*. No initial stage with a high rate of oxygen absorption was observed. It seems reasonable to assume that such a region is caused by easily oxidizable nonrubber materials which in this case had been previously extracted from the samples.

The diamine was consumed during the constant rate stage, Curve *B*, indicating that this region is controlled by the antioxidant. The decrease in diamine concentration was nearly linear down to low concentrations, where deviations from linearity were observed. Extrapolation of the linear part to zero concentration and comparison of the time OX with the duration of the

constant rate stage OY showed that OY was about twice OX. (In faster oxidizable vulcanizing systems such as sulfur + DPG, e.g., OY was found to be somewhat less than twice OX). A determination of the rate of oxygen uptake $\Delta O_2/\Delta t$ and the rate of diamine (DA) consumption $\Delta DA/\Delta t$ allowed us to calculate $\Delta O_2/\Delta DA$. This ratio gives the number of oxygen molecules absorbed per molecule of diamine consumed which was constant in the linear range. This ratio was found to be 5–6 and nearly independent of the nature of the curing system, the presence of carbon black, the initial concentration of the amine, and the oxidation temperature. Since OY was found to be twice OX, the total amount of oxygen absorbed during the induction period corresponded to 10–12 times the molar amount of initial diamine concentration. That OY is twice OX can be explained by the fact that each diamine molecule is able to terminate two oxidation chains.

The main reaction product of the inhibitor was found to be unextractable and probably bound to the rubber. The nitrogen content of the rubber samples increased almost correspondingly with the consumption of the diamine. The only extractable reaction product formed was the quinone diimine which was found in small quantities (up to 3% of the initial amine concentration) during the first part of the oxidation. Kuzminskiĭ and coworkers[4] have reported in a series of papers about the oxidation of butadiene polymers in the presence of phenyl-2-naphthylamine. It was established by them that the antioxidant was used up and was attached to the rubber molecule. The rate of the inhibitor consumption was found to be constant and equal to the rate of combination with rubber. At higher initial inhibitor concentrations, a more complex situation was observed.

Figure 2 illustrates the effect of the vulcanizing system on oxygen absorption

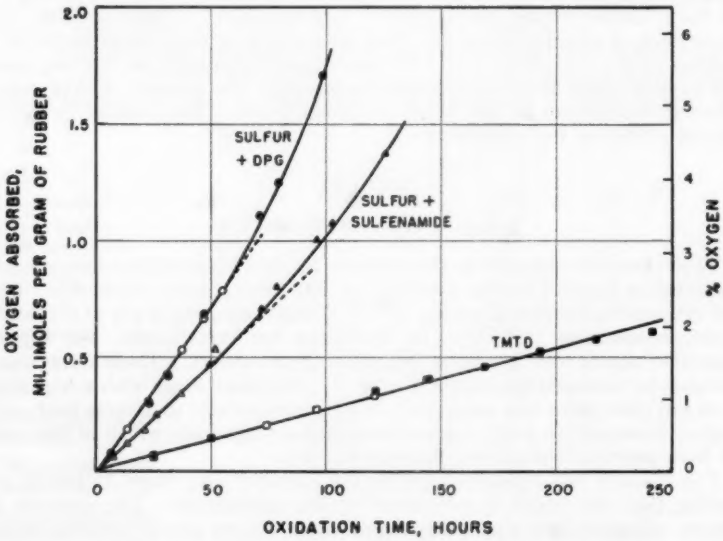


FIG. 2.—Oxygen absorption of different vulcanizates containing 2.60 phr of diphenyl-*p*-phenylenediamine at 100° C.

at 100° C. Samples with identical crosslinking density were prepared using different curing systems. (Swelling values: 3.9–4.1 grams of benzene per gram of rubber network). Two were sulfur-accelerator systems 2-(morpholinothio)-benzothiazole and diphenyl guanidine and the third one was a sulfur-free tetramethylthiuram disulfide vulcanizate, Table I. To eliminate any effect of vulcanization residues and natural inhibitors, the samples were extracted prior to introducing the diamine by swelling. All samples contained the same initial concentration of DPPD, namely 26 ± 2 mg per gram of rubber. The open points in Figure 2 represent the values of individual samples oxidized for a certain time. The filled points correspond to values obtained with one sample which was oxidized until a pronounced autocatalytic region was reached. It is seen that good reproducibility of the measurements was observed. The

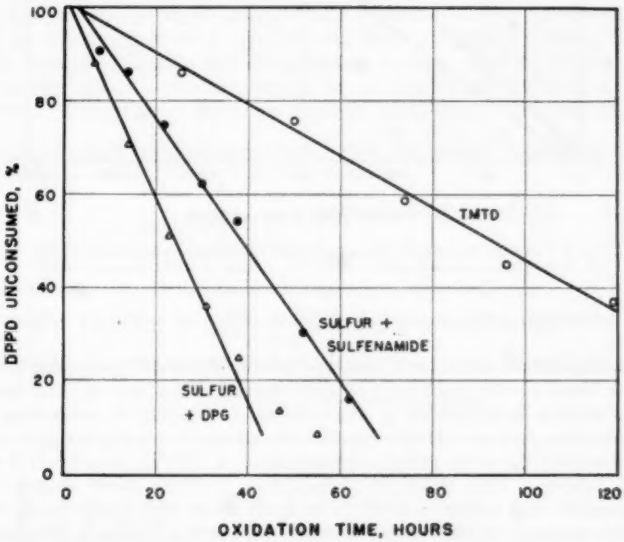


FIG. 3.—Consumption of diphenyl-p-phenylenediamine in different vulcanizates at 100° C. Original concentration, 2.60 phr.

results show that the oxidizability depended to a large extent on the amount of bound sulfur which increased for the curing systems in the order TMTD- < sulfur + sulfenamide- < sulfur + DPG-. The consumption of DPPD is shown in Figure 3. The rate of diamine consumption corresponded with the rate of oxygen absorption. In easily oxidizable systems, e.g., sulfur + DPG, a rapid consumption of the diamine (DA) was observed. A calculation of the quotient $\Delta O_2/\Delta DA$ in the constant rate region illustrates that this ratio was nearly identical in the three systems although their oxidizability varied greatly. The quotient $\Delta O_2/\Delta DA$ was found to be close to six for all three systems. This must be considered as evidence that the oxidation takes place on the rubber hydrocarbon and not at certain sulfur-containing linkages. At any rate, the latter reaction does not take place to any appreciable degree. Shelton[5] has pointed out that the increased rate of oxidation with higher levels of combined

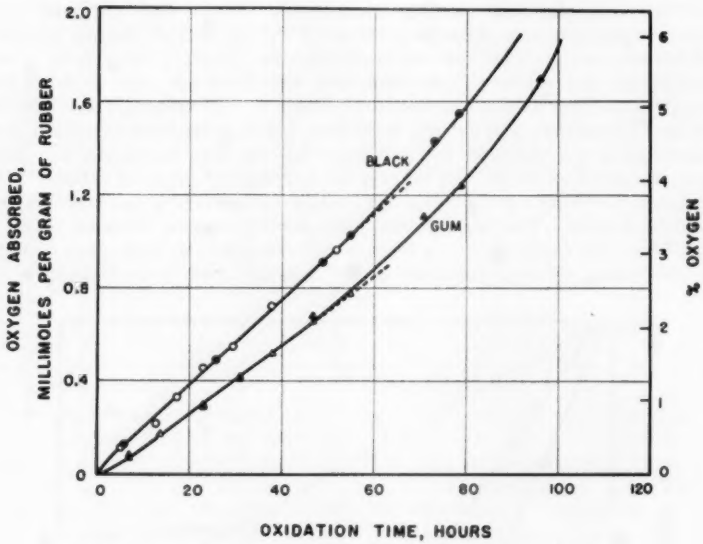


FIG. 4.—Oxygen absorption of gum and black vulcanizates containing 2.75 phr of diphenyl-p-phenylenediamine at 100° C. (Sulfur + DPG curing system.)

sulfur is associated with an activating effect of bound sulfur on adjacent C-H groups.

Extensive studies have been reported in the literature[5] exploring the effect of carbon black on the oxidation of elastomers. They reveal that the effect of carbon black is quite complex. We compared vulcanizates containing 50 phr of high abrasion furnace (HAF) black with otherwise analogous gum vulcanizates containing the same initial concentration of DPPD, namely 27.5 mg per gram of rubber. Two different vulcanizing systems were chosen—sulfur + sulfenamide and sulfur + DPG. In both cases the black stock reacted faster with oxygen at 100° C by a factor of 1.3–1.4. This is illustrated in Figure 4 for the sulfur + DPG curing system. Simultaneously, the rate of amine consumption was accelerated also by a factor of 1.35 as shown in Figure 5. This demonstrates that the molar ratio $\Delta O_2/\Delta DA$ was unchanged by the black. Adsorption or reaction of the diamine on the carbon black surface (and as a consequence unavailability of the inhibitor) or promotion of a direct oxidation of the diamine to inactive products can be of only minor importance.

The rates of oxygen absorption and diamine consumption of the constant rate stages as well as the molar ratio $\Delta O_2/\Delta DA$ are listed in Table II. The table shows that analogous results were obtained in all vulcanizing systems listed. A more complicated situation was observed only in peroxide vulcanizates (Mixture 1, Table I), where the corresponding diimine was found in larger quantities (maximum amount 15% of the initial diamine concentration). Since the diimine reacts with natural rubber[6] with reformation of the diamine in about 70% yield[7], we observe here a regeneration of the inhibitor which complicated the kinetic results.

The question now arises why a nearly zero order consumption of the diaryl-

TABLE II

OXYGEN ABSORPTION AND DIAMINE CONSUMPTION AT 100° C IN DIFFERENT NATURAL RUBBER VULCANIZATES (INITIAL CONCENTRATION OF DPPD 2.6 ± 0.2 PHR)

Vulcanizing system[a]	$\Delta O_2/\Delta t$ [millimoles/g rubber × hour]	$\Delta DA/\Delta t$ [millimoles/g rubber × hour]	$\Delta O_2/\Delta DA$ (molar)
TMTD (sulfurless) (gum)	2.5×10^{-3}	0.49×10^{-3}	5.1
Sulfur + sulfenamide (gum)	9.2×10^{-3}	1.55×10^{-3}	5.9
Sulfur + DPG (gum)	14.0×10^{-3}	2.35×10^{-3}	5.95
Sulfur + sulfenamide (black)	12.75×10^{-3}	2.10×10^{-3}	6.05
Sulfur + DPG (black)	18.5×16^{-3}	3.15×10^{-3}	5.9

[a] See Table I.

p-phenylenediamines was observed. It might be envisioned that low solubility of the diamines in natural rubber is responsible. The observance of similar kinetic conditions in other elastomers[8] with greater solubility for these diamines as well as the dependence of the rate on the vulcanizing system, Table II, indicate that solubility is not the decisive factor. Rather, the reaction in which the diamine is consumed should be responsible for the observed kinetic conditions. A number of reactions must be considered in this respect[5].

1. Direct oxidation of the antioxidant with the formation of stable oxidation products or chain initiating free radicals.

$$(1) \quad AH + O_2 \begin{cases} \longrightarrow \text{stable oxidation products} \\ \longrightarrow A\cdot + HO_2\cdot \end{cases}$$

2) Reaction with peroxy radicals leading to termination

$$(2) \quad AH + RO_2\cdot \longrightarrow \text{leading to termination}$$

3) Peroxide decomposition with the formation of stable products

$$(3) \quad ROOH + AH \longrightarrow \text{stable products}$$

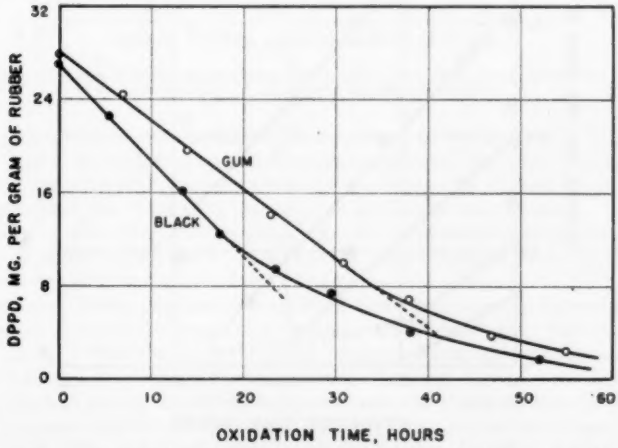


FIG. 5.—Consumption of diphenyl-*p*-phenylenediamine in gum and black vulcanizates at 100° C. (Sulfur + DPG curing system.) Original concentration, 2.75 phr.

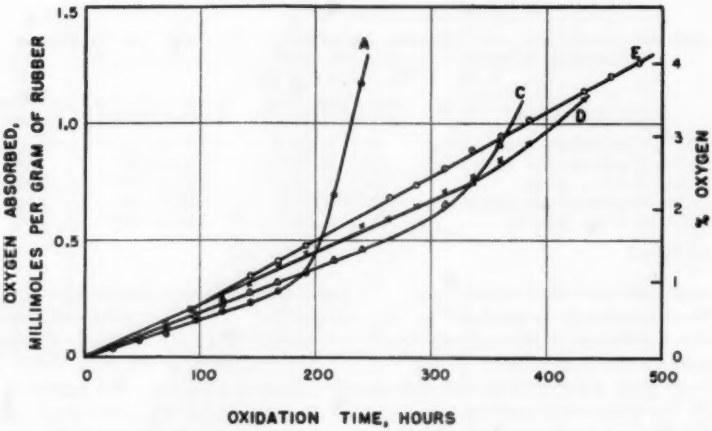


FIG. 6.—Oxygen absorption of TMTD gum vulcanizates containing various concentrations of N,N′-di-*p*-tolyl-*p*-phenylenediamine at 100° C. (*A*—0.635 phr, *C*—1.98, *D*—3.05, *E*—4.55.)

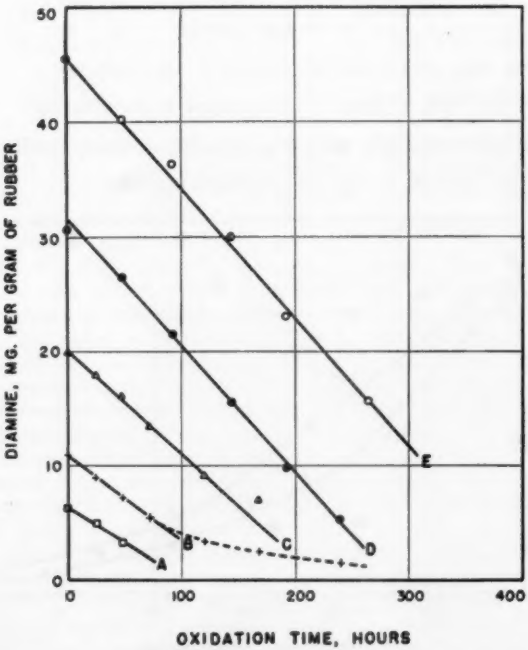


FIG. 7.—Consumption of di-*p*-tolyl-*p*-phenylenediamine in TMTD gum vulcanizates at 100° C. (*A*—0.635 phr, *B*—1.10. *C*—1.98, *D*—3.05, *E*—4.55.)

If the antioxidant AH would be consumed predominantly according to reaction (1), the diamine consumption should be of first order under the chosen experimental conditions (constant oxygen pressure). Peroxide decomposition, reaction (3), does not seem likely to be the predominant reaction since chain scission should not be expected. Nevertheless, chain scission is a noticeable consequence of the oxidation of natural rubber even in the presence of diaryl-*p*-phenylenediamines. We found that the amount of sol rubber formed increased with increasing oxygen uptake. These considerations suggest that diaryl-*p*-phenylenediamines are mainly consumed in a termination mechanism, reaction (2), which is not understood in detail at the present time. The low value of six found for the molar ratio $\Delta O_2/\Delta DA$ indicates that the kinetic chain length must be low. Bevilaqua[9] has reported in a series of papers that the chain scission efficiency of Hevea by molecular oxygen increases rapidly with increasing temperature to a limiting value of about six molecules of O_2 per scission. This evidently means that six molecules of oxygen are needed for one oxidation

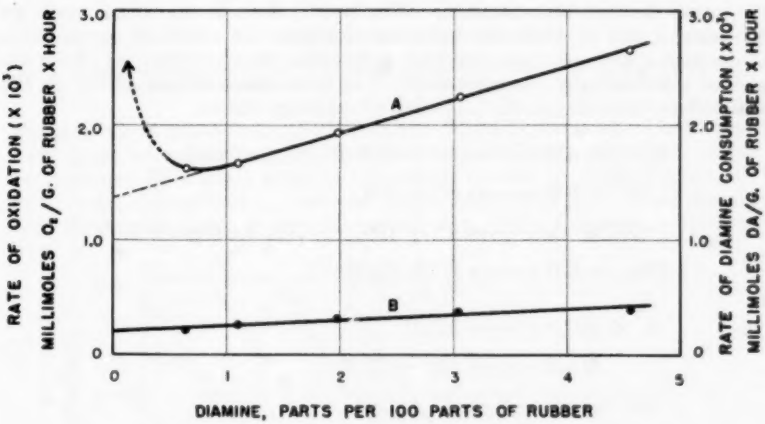


FIG. 8.—Effect of initial concentration of di-*p*-tolyl-*p*-phenylenediamine on the rate of oxygen absorption, *A*, and rate of diamine consumption, *B*.

cycle including one chain scission which according to Tobolsky and Mercurio[10] occurs in the termination step. Our own results could then be interpreted to mean that diaryl-*p*-phenylenediamines are reducing the kinetic chain length to one, provided the diamine is present in a sufficient concentration.

A study of the effect of the initial diamine concentration on the rate of oxidation is shown in Figure 6. The results were obtained with TMTD gum compounds containing different initial concentrations of di-*p*-tolyl-PD. In the range we have shown, the samples oxidized more rapidly with increasing concentration of the antioxidant. The duration of the inhibition period did not increase linearly with the initial diamine concentration, but approximately as the square root. A linear relationship existed, however, between the amount of oxygen absorbed during the inhibition period and the initial diamine concentration. The consumption of the diamine likewise depended on the initial diamine concentration, the rate increasing with increasing diamine concentration, Figure 7. It has been shown previously that certain amine antioxidants ex-

hibit an optimum concentration at which the rate of oxidation has a minimum value in the constant rate region[11]. Addition of either more or less antioxidant results in a more rapid oxidation. The same was true for di-*p*-tolyl-PD as illustrated in Figure 8 where the initial oxidation rates are plotted against the initial amine concentration, curve *A*. The minimum value was found at 0.8 phr. If no antioxidant is present, the rate was extremely high. A steep decrease of the rate was observed in the first part of the curve. After passing through a minimum, the rate then increased slowly. Curve *B* represents the rate of diamine consumption as a function of the initial diamine concentration. The consumption of the diamine depended much less on the initial diamine concentration than did the rate of oxygen uptake, the ratio of the two values being equal to 6. The appearance of a minimum in Curve *A* indicates that two different rate equations are observed for these two regions of the curve (before and after the minimum). Before the minimum was reached, the rate decreased rapidly with increasing diamine concentration. After passing the minimum the situation changed, now the rate of oxidation increased with the initial diamine concentration. This latter region is the range which we investigated and in which six molecules of oxygen are absorbed per molecule of diamine consumed. An optimum antioxidant concentration has been explained previously by chain transfer[11, 12] or by a direct oxygen attack on the antioxidant[11] resulting in the initiation of oxidation chains.

$$RO_2^{\cdot} + AH \longrightarrow A^{\cdot} + ROOH \quad \text{Chain transfer}$$

$$A^{\cdot} + RH \longrightarrow R^{\cdot} + AH$$

$$AH + O_2 \longrightarrow A^{\cdot} + HO_2^{\cdot} \quad \text{Direct oxygen attack}$$

$$HO_2^{\cdot} + RH \longrightarrow R^{\cdot} + H_2O_2$$

or

$$A^{\cdot} + HO_2^{\cdot} \longrightarrow AO_2H$$

$$AO_2H \longrightarrow AO^{\cdot} + HO^{\cdot}$$

$$HO^{\cdot} + RH \longrightarrow R^{\cdot} + H_2O$$

Since the antioxidant radicals $A^{\cdot}$ are highly stabilized by resonance, it seems doubtful whether they are able to initiate oxidation chains. The situation is different, however, with the more reactive hydroperoxy- or hydroxy-radicals formed by direct oxygen attack.

That two or more reactions compete for the consumption of the diamine was confirmed by the finding of a fractional order. A plot of the logarithm of the initial rate of diamine consumption vs. the logarithm of the initial diamine concentration gave a reaction order of 0.35 with respect to the diamine.

In order to find a correlation of antioxidant efficiency with the structure of diaryl-*p*-phenylenediamines, TMTD (sulfurless) gum vulcanizates containing equimolar amounts of various diamines (ca. 9.5 millimoles per 100 grams of rubber) were oxidized under identical conditions. The oxygen absorption curves at 100° C are shown in Figure 9. The curves are shifted on the abscissa for a certain distance to obtain a clearer picture. In the presence of diphenyl-PD, phenyl-*p*-tolyl-PD, and di-*p*-tolyl-PD, a linear oxygen uptake was observed. Since the three lines are parallel, the rates were identical, indicating equal efficiency of these three diamines under our experimental conditions. In

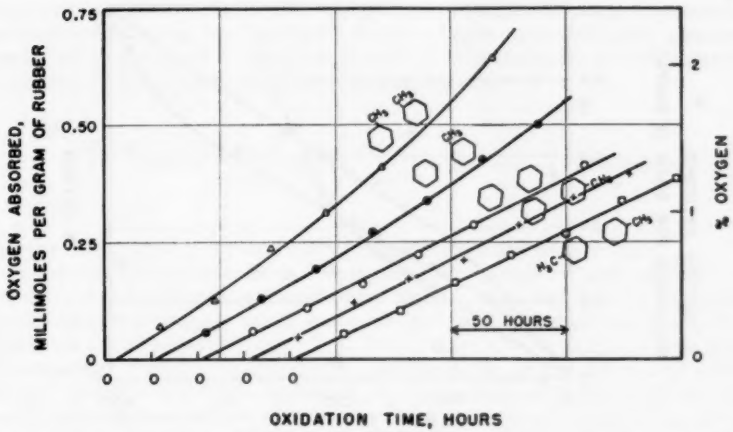


FIG. 9.—Oxygen absorption of TMTD vulcanizates containing equimolar amounts of various diaryl-*p*-phenylenediamines at 100° C. (9.5 millimoles per 100 grams of rubber.)

the presence of phenyl-*o*-tolyl-PD and di-*o*-tolyl-PD, deviations from linearity were observed. The lower efficiency of the *o*-tolyl derivatives can probably be explained by a steric effect of the methyl group. A determination of the initial rates showed that the ratio $\Delta O_2/\Delta DA$ was nearly six for these somewhat less efficient diamines during the initial part of the oxidation. This ratio,

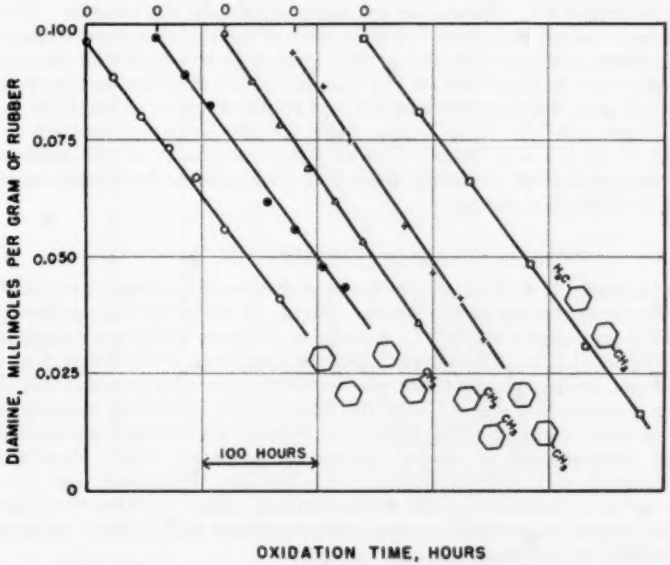


FIG. 10.—Consumption of diaryl-*p*-phenylenediamines in TMTD gum vulcanizates at 100° C. Original concentration 9.5 millimoles per 100 grams of rubber.

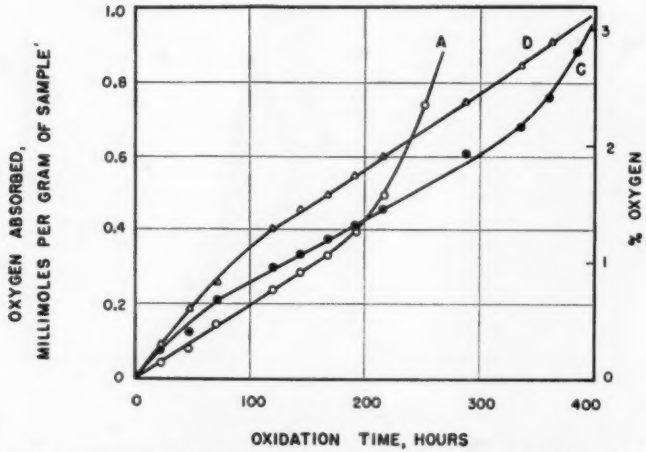


FIG. 11.—Oxygen absorption of TMTD vulcanizates containing various concentrations of N-isopropyl-N′-phenyl-*p*-phenylenediamine at 100° C. (*A*—0.65 phr, *C*—1.98, *D*—2.90.)

however, increased with increasing oxidation time. It should be pointed out that the antioxidant efficiency was also found to be a function of the temperature. Samples containing phenyl-*o*-tolyl-PD absorbed oxygen with a constant rate at 80° (but not at 100°) illustrating that the efficiency increased with decreasing temperature. The consumption of the various diamines is shown in Figure 10. The curves are again shifted on the abscissa. Parallel lines were obtained indicating identical rates of the diamine consumption.

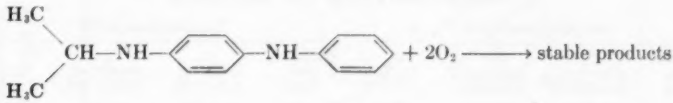
An overall activation energy of 22.5 kcal/mole was found for the oxygen uptake but only 21 kcal/mole for the diamine consumption during the oxidation of TMTD gum vulcanizates containing 2.5 phr of phenyl-*o*-tolyl-PD in the range of 80°–120° C. The higher value for the oxidation reaction is not believed to be the true value. Due to a lower efficiency of the inhibitor at higher temperatures, it is usually difficult to determine the true initial oxidation rate of the induction period.

DIALKYL- AND ALKYL-ARYL-*p*-PHENYLENEDIAMINES

The addition of dialkyl- or alkyl-aryl-*p*-phenylenediamines as antioxidants had a pronounced effect on the results. Figure 11 shows the oxygen absorption of TMTD gum stocks at 100° C, containing different initial concentrations of isopropylphenyl-PD. The oxygen absorption curves are composed of at least three stages, initial, constant rate, and autocatalytic. An investigation of the diamine consumption showed that the diamine was consumed approximately by a first order reaction. This is shown in Figure 12 where the logarithm of the diamine concentration is plotted against the oxidation time. Parallel lines were obtained with different initial concentrations, indicating that the rate constant was independent of the concentration. Since we were working with constant oxygen pressure, these results are consistent with a direct oxidation of this diamine by oxygen.

An investigation of the direct oxidation of isopropylphenyl-PD (in the absence of rubber) showed that this material was indeed readily oxidizable.

The results are given in Table III. Surprisingly enough, the reaction proceeded stoichiometrically as the quotient, moles oxygen absorbed/mole diamine consumed, was found to be constant, namely, 2.04 in the range we investigated. Obviously we are dealing with the following reaction:



whereby the nature of the oxidation products is not presently known.

After establishing these facts, it was possible to obtain a "true" oxygen absorption curve by correcting the measured values. This was done by subtracting the amount of oxygen which was consumed by direct oxidation of the diamine from the measured values. E.g., from Figure 12, Curve *C*, it is seen that the amount of diamine consumed after 144 hours was 19.8 − 2.0 = 17.8 milligrams, 17.8/226 = 0.0788 millimole of isorpopylphenyl-PD. 0.0788 × 2 = 0.158 millimole of oxygen absorbed by the diamine and to be deducted from the measured value of oxygen absorption. From Figure 11, Curve *C*, the measured value of oxygen absorption was 0.352/0.88 = 0.396 millimole (where 88.8 is the % rubber hydrocarbon in the sample). 0.396 − 0.158 = 0.238 millimole of oxygen, the corrected value. The "true" oxygen absorption

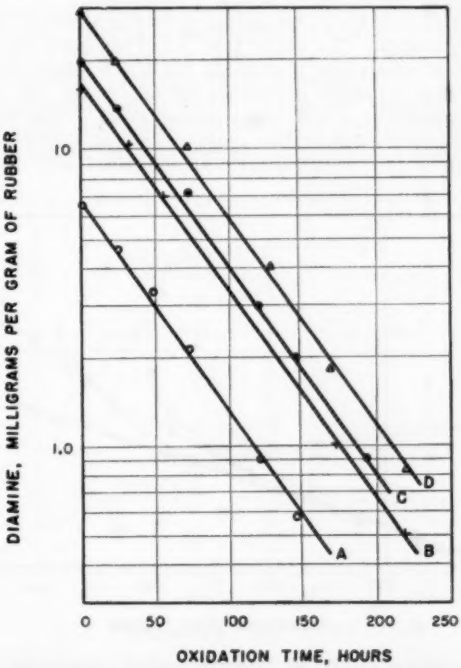


FIG. 12.—Consumption of N-isopropyl-N′-phenyl-*p*-phenylenediamine in TMTD gum vulcanizates at 100° C. (*A*—0.65 phr, *B*—1.58, *C*—1.98, *D*—2.90.)

TABLE III

DIRECT OXIDATION OF N-ISOPROPYL-N′-PHENYL-*p*-PHENYLENEDIAMINE AND N, N′-BIS (1-METHYLHEPTYL) -*p*-PHENYLENEDIAMINE IN OXYGEN AT 90° C AND 740 MM. INITIAL DIAMINE CONCENTRATION: ISOPROPYLPHENYL-PD 1.95 MILLIMOLES DIMETHYLHEPTYL-PD 1.42 MILLIMOLES

Isopropylphenyl-PD				Dimethylheptyl-PD			
Oxidation time, hours	O_2 absorbed, millimoles	DA consumed, millimoles	O_2/DA (molar)	Oxidation time, hours	O_2 absorbed, millimoles	DA consumed, millimoles	O_2/DA (molar)
12	0.392	0.192	2.04	5½	0.458	0.283	1.62
29	0.866	0.419	2.07	8	0.777	0.497	1.56
47	1.33	0.670	1.99	14	1.40	0.815	1.72
75	1.58	0.764	2.07	29	2.22	1.252	1.77
167	2.03	0.997	2.04	70	3.03	1.413	2.15

curves are shown in Figure 13. Again we find that the oxygen absorption proceeded linearly at the beginning. All points fall on the same line with the exception of the values found in the presence of the highest amine concentration, pointing to a possible dependence of the rate on the concentration. We observed here the interesting fact that the diamine itself does not act as an antioxidant (since it was consumed predominantly by direct oxidation) but that one of its oxidation products assumes the function of an antioxidant. The rate of oxidation in the constant rate region was quite low showing that the oxidation product in question is a powerful antioxidant.

We had expected that the direct oxidation of this amine would be independent of the curing system. To verify this, we investigated the oxidation of a sulfur + DPG gum compound containing 2.5 phr of isopropylphenyl-PD expecting that in such a readily oxidizable curing system, the direct oxidation would be superimposed on a zero order consumption. This was not the case, however, as the diamine consumption again was a first order reaction but with a higher rate constant (3.1×10^{-2} hour^{-1} as compared with 1.6×10^{-2} hour^{-1}

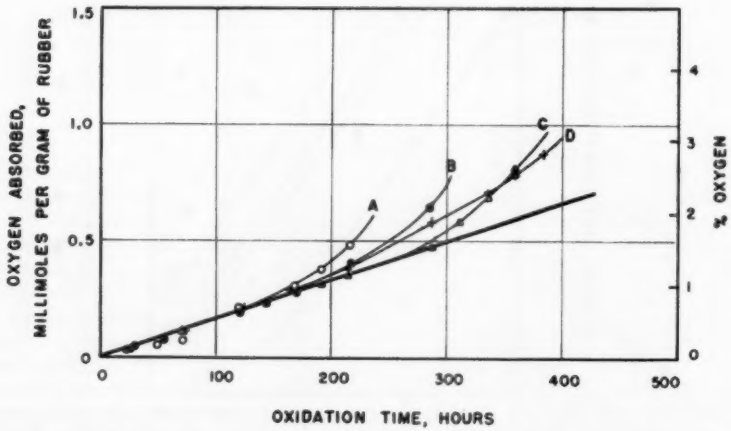


FIG. 13.—Oxygen absorption of TMTD gum vulcanizates corrected for the consumption of oxygen by N-isopropyl-N′-phenyl-*p*-phenylenediamine at 100° C. (*A*—0.65 phr, *B*—1.58, *C*—1.98, *D*—2.90.)

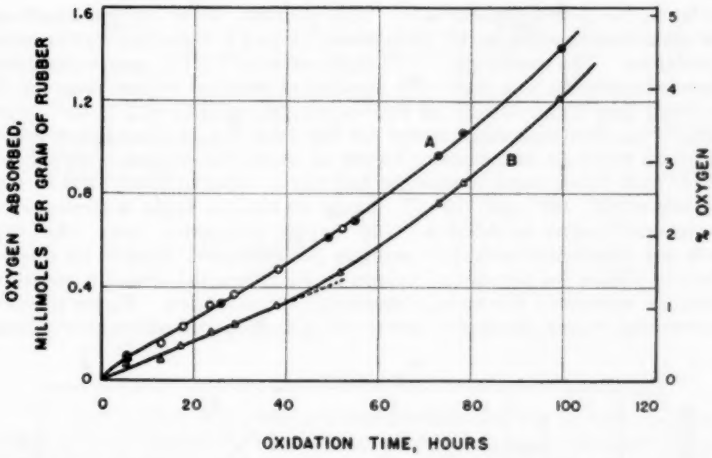


FIG. 14.—Oxygen absorption, *A*, and corrected oxygen absorption, *B*, of gum vulcanizates containing N-isopropyl-N′-phenyl-*p*-phenylenediamine at 100° C. (Sulfur + DPG curing system.) Original concentration, 2.50 phr.

in TMTD gum compounds). Figure 14 shows the oxygen uptake as a function of the oxidation time. Curve *A* represents the measured values and Curve *B* the corrected values (obtained by subtracting the amount of oxygen which was needed for the direct oxidation of the diamine).

Dialkyl-*p*-phenylenediamines—we used dimethylheptyl-PD as an example—behaved similarly to N-alkyl-N′-aryl-*p*-phenylenediamines. Dimethylheptyl-PD was easily oxidized as seen from Table III, being much faster than

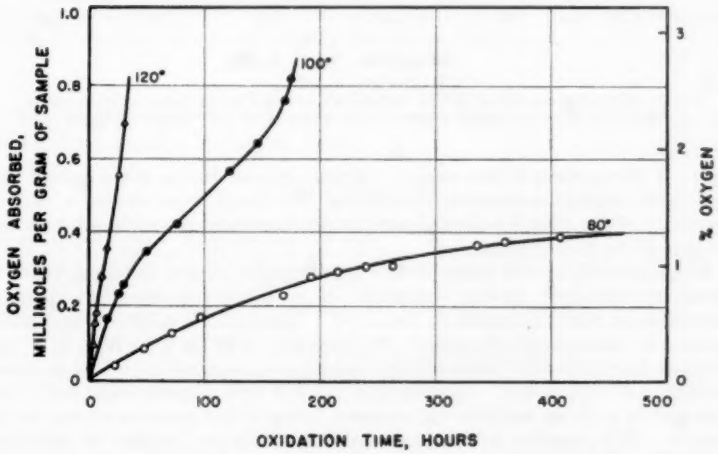


FIG. 15.—Oxygen absorption of TMTD vulcanizates containing 3.25 phr of N,N′-bis(1-methylheptyl)-*p*-phenylenediamine.

was found for isopropylphenyl-PD. The quotient, moles oxygen absorbed/mole diamine consumed, varied from about 1.5 to 2.2 depending on the extent of oxidation. The consumption of the diamine in TMTD gum vulcanizates proceeded according to a first order reaction at constant oxygen pressure, the rate being four times as high as for isopropylphenyl-PD (6.2×10^{-2} hour^{-1} at 100° C). The activation energy for the oxidation of dimethylheptyl-PD was found to be 18 kcal./mole. Figure 15 shows the oxygen absorption of TMTD gum vulcanizates containing 3.25 phr of dimethylheptyl-PD at temperatures of 80°, 100° and 120° C. Again we tried to apply a correction for the measured values to obtain a "true" oxygen absorption curve. Although it was not completely correct to multiply the consumed diamine by a factor of two to obtain the amount of oxygen to be subtracted from the measured values, we considered this to be a reasonable simplification. Figure 16 shows the corrected oxygen absorption curves which again began with a nearly linear

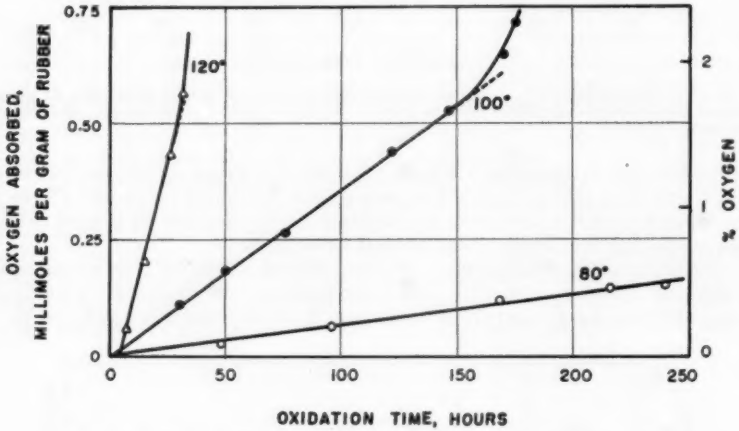


FIG. 16.—Oxygen absorption of TMTD vulcanizates corrected for the consumption of oxygen by N,N'-bis(1-methylheptyl)-*p*-phenylenediamine, original concentration, 3.25 phr.

stage. A comparison of the rates of oxygen uptake during the constant rate stage with analogous samples containing the diaryl type shows a definite superiority of the diaryl-*p*-phenylenediamines in respect to oxidation rate and duration of the inhibition period.

A comparison of the rates of the consumption of the different types of *p*-phenylenediamines during oxidation of a tetramethylthiuram disulfide vulcanizate at 100° C is made in Table IV. The time for a 50% consumption was used to characterize the rates. For di-*p*-tolyl-PD the time for a 50% consumption increased with higher initial diamine concentration. This increase, however, was not linear. Isopropylphenyl-PD and dimethylheptyl-PD are consumed by a direct reaction with oxygen, being of first order in respect to the diamine. This reaction is relatively fast, especially in the case of dimethylheptyl-PD. The time for a 50% consumption was found to be independent of the initial concentration of isopropylphenyl-PD.

TABLE IV

CONSUMPTION OF *p*-PHENYLENEDIAMINES IN TMTD GUM VULCANIZATES (IN OXYGEN AT 100° C)

p-Phenylenediamine	Initial concentration, phr	Time for 50% consumption, hours
N,N′-di-*p*-tolyl-	0.64	52
	1.10	72
	1.98	111
	3.05	134
	4.55	202
N-Isopropyl-N′-phenyl-	0.65	44
	1.58	46
	1.98	44
	2.90	44
N,N′-bis(1-methylheptyl)-	3.25	11

SUMMARY

The consumption of various *p*-phenylenediamines during the oxidation of natural rubber vulcanizates has been investigated in the temperature range of 80–120° C. Oxygen absorption was used to follow the oxidation.

Diaryl-*p*-phenylenediamines were consumed mainly in a termination reaction during the constant rate region of the oxygen absorption, where five to six molecules of oxygen were absorbed per molecule of diamine consumed. The constant rate stage of the oxygen uptake was found to be about twice as long as the time of the constant rate consumption of the diamine, indicating that the reaction product also possessed antioxidant activity. The effect of the nature of the curing system, carbon black, structure of the diamine, initial concentration of the diamine, and temperature of oxidation were studied.

Dialkyl- and alkyl-aryl-*p*-phenylenediamines were consumed predominantly by a direct, relatively fast reaction with oxygen, the rate being dependent on the structure of the diamine and also on the nature of the curing system. The oxidation products formed exhibited antioxidant activity, those of N-isopropyl-N′-phenyl-*p*-phenylenediamine being particularly effective.

ACKNOWLEDGMENT

The authors wish to express their sincere appreciation to Dr. J. Reid Shelton for a number of helpful discussions.

REFERENCES

[1] Shelton, J. R. and Winn, H., *Ind. Eng. Chem.* **38**, 71 (1946).
[2] Lorenz, O. and Parks, C. R., details to be published.
[3] Piccard, J., *Ann.* **381**, 351 (1911); *Ber.* **46**, 1843 (1913); *Ber.* **59**, 1438 (1926).
[4] Kuzminskii, A. S. and Lezhnev, N. N., RUBBER CHEM. & TECHNOL. **28**, 412 (1955); Angert, L. G. and Kuzminskii, A. S., *J. Polymer Sci.* **32**, 1 (1958).
[5] Shelton, J. R., RUBBER CHEM. & TECHNOL. **30**, 1267 (1957).
[6] Fisher, H. L., *Ind. Eng. Chem.* **31**, 1381 (1939).
[7] Parks, C. R. and Lorenz, O., unpublished.
[8] Lorenz, O., Lichty, J. G. and Parks, C. R., unpublished.
[9] Bevilaqua, E. M., *J. Am. Chem. Soc.* **77**, 5394 (1955); *ibid.* **77**, 5396 (1955).
[10] Tobolsky, A. V. and Mercurio, A., *J. Am. Chem. Soc.* **81**, 5535 (1959).
[11] Shelton, J. R. and Cox, W. L., *Ind. Eng. Chem.* **46**, 816 (1954).
[12] Bickel, A. F. and Kooyman, E. C., *J. Chem. Soc.* 2215 (1956).

THE INFLUENCE OF HIGH-ACTIVITY SILICA UPON THE THERMAL AGING OF LATEX VULCANIZATES CURED BY THIURAM COMPOUNDS *

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INTRODUCTION

Once it had been shown that high-activity silica, even in comparatively small additions, improves the aging resistance of latex vulcanizates by many times[1], and that also an effect similar to that of a coactivator is set up by the interaction of high-activity silica with age resistors, ultra-accelerators and atmospheric oxygen in latex mixtures[2], a like effect was to be expected in sulfur-free latex vulcanizates crosslinked by thiuram compounds. In order to get comparable data it was necessary in the first place to get sulfur-free latex mixtures giving vulcanizates with starting properties in the same order of value as those of latex vulcanizates with the classical sulfur recipe. In addition it was necessary also to develop stocks from which threads could be extruded by the well-known two-stage method[1], since the investigations mentioned at the beginning were carried out exclusively on vulcanized threads, which lend themselves particularly well to determinations of tensile strength, elongation at break and tensile stress. Above all an attempt was made to manage with vulcanization temperatures below 100° C. To make this possible a thiuram compound active at relatively low temperatures had to be used. Here we had the opportunity of using DPTT (dipentamethylenethiuram tetrasulfide, Tetrone A), which the manufacturers (Du Pont) designate, alone among their thiuram accelerators, as "very active", and which J. Willums referred to in a German journal as far back as 1944[3].

DEVELOPMENT OF A SUITABLE THURAM RECIPE

Even in sulfur-containing formulas it was possible to establish the higher activity of dipentamethylenethiuram tetrasulfide as compared with the best known of the thiuram accelerators, tetramethylthiuram disulfide (TMTD). At the same time it was found that a combined addition of dipentamethylenethiuram tetrasulfide and tetramethylthiuram disulfide was more effective than either of these thiuram compounds alone, as the properties in Table 1 show. The permanent set as a measure of the degree of vulcanization is shown by the so-called 300/300 value. This is obtained on plotting the stress-strain-retraction curve up to 400% elongation by dividing the stress of extension by the stress of retraction at 300% elongation. The lower this 300/300 value, the smaller the hysteresis loop and thus also the permanent set.

The higher activity of DPTT (dipentamethylenethiuram tetrasulfide) as compared with TMTD showed itself also in sulfur-free latex stocks, likewise the advantage of using TMTD as a second accelerator to DPTT. Table 2

* Translated by R. J. Moseley from *Kautschuk und Gummi* 13, WT1-12 (1960); RAPRA translation 852. To save space many of the figures in the original article are not included in this translation.

TABLE 1

INITIAL PROPERTIES OF SULFUR CROSSLINKED, THIURAM-ACCELERATED VULCANIZATES (SEE NOTE)

	1305		1306		1307	
Colloidal sulfur	2.0		2.0		2.0	
TMTD	0.5		—		0.25	
DPTT	—		0.8		0.4	
Diethylamine	0.5		0.5		0.5	
ZnO	2.5		2.5		2.5	
Cure time, hours, air, 100° C	T.S.	E/B	T.S.	E/B	T.S.	E/B
1	476	879	338	960	520	791
2	451	815	466	806	487	768
3	425	792	421	806	456	756
4	376	768	419	789	399	741
1.5*	380	834	390	983	463	774
1.5	464	840	422	825	503	779
	SV	300/300	SV	300/300	SV	300/300
1	22.2	2.18	15.5	3.42	33.8	1.73
2	26.0	1.74	26.5	1.85	36.1	1.67
3	27.6	1.59	28.3	1.47	36.1	1.57
4	28.8	1.50	31.3	1.48	36.9	1.56
1.5*	20.7	1.91	16.3	2.48	32.3	1.62
1.5	24.3	1.90	23.9	2.48	35.2	1.70

ABBREVIATIONS USED IN TEXT AND TABLES: DPTT, Dipentamethylenethiuram tetrasulfide; TMTM, Tetramethylthiuram monosulfide; TMTD, Tetramethylthiuram disulfide; MBT, Mercaptobenzthiazole; MBTZn, Zinc salt of mercaptobenzthiazole; Hexa, Hexamethylene tetramine; DDA, DDA Antiager (Bayer); ARW, DNP Antiager (Bayer) (Di-β-naphthyl-*p*-phenylene diamine); BKF, BKF Antiager (Bayer) (2,2′-methylene-bis-(4-methyl-6-*tert*-butyl phenol); MBIZn, Zinc salt of mercaptobenzimidazole; ZnO, Zinc oxide; T.S., Tensile strength, in kg/sq cm; E/B, Elongation at break, %; SV, Stress value at 400% elongation, kg/sq cm; Tens. Prod., Tensile product (product of tensile strength and elongation at break).

The mix compositions in the Tables are given in each case in % reckoned against dry rubber.

* 95° C.

gives figures for two vulcanizates with TMTD and DPTT, respectively, as the main crosslinking agent, and with MBT and hexa as activators. In Table 3 we give the properties of three vulcanizates with DPTT as the main crosslinking agent and MBT or MBT plus TMTD as activators. The two vulcanizates 1309 and 1310 with TMTD not only have higher T.S. but also higher E/B. From Table 4 it is seen that as activator for the combination DPTT-TMTD-

TABLE 2

INITIAL PROPERTIES OF SULFUR-FREE, THIURAM-CROSSLINKED VULCANIZATES

	1317			1318		
TMTD	2.6			—		
DPTT	—			2.6		
MBT	0.5			0.5		
Hexa	0.5			0.5		
ZnO	3.0			3.0		
Cure time, hours, air, 100° C	T.S.	E/B	SV	T.S.	E/B	SV
1	103	1058	10.2	209	715	18.9
2	—	—	—	248	606	34.0
3	—	—	—	242	558	37.8
4	29	1028	3.6	240	544	41.4
3 (90° C)	—	—	—	253	604	30.4

TABLE 3

INITIAL PROPERTIES OF VULCANIZATES OF STOCKS WITH DIPENTAMETHYLENE-THIURAM TETRASULFIDE AS MAIN CROSSLINKING AGENT (I)

	1308		1309		1310	
DPTT	1.5		1.0		1.0	
MBT	1.5		1.0		1.0	
TMTD	—		1.0		1.0	
Diethylamine	—		—		0.5	
ZnO	3.0		3.0		3.0	
Cure time, hours, air, 100° C	T.S.	E/B	T.S.	E/B	T.S.	E/B
1	258	675	294	845	279	813
2	269	635	331	718	354	733
3	288	653	347	690	295	654
4	269	636	327	665	325	661
	SV	300/300	SV	300/300	SV	300/300
1	26.8	2.18	18.4	2.24	18.4	2.24
2	29.1	2.17	27.5	2.11	28.5	2.02
3	30.1	2.05	31.4	1.97	32.8	1.98
4	30.6	1.93	33.7	2.01	33.5	1.97

MBT is to be replaced in part by hexa in the molar ratio 1:1. As to how far we can get a full cure at temperatures of only 90° C instead of 100°, this is shown by the stage heatings of vulcanizate 1316, where it is noteworthy that the T.S. was higher, while with practically equal E/B and equal SV, than with heating at 100°. The fact that it is better for the quality of the vulcanizate to use a small amount of an effective accelerator combination than to use a high amount of less effective combination is seen from the figures for vulcanizates 1319 and 1322 in Table 5. The two stocks are based on the same vulcanizing agent dispersion, only with the difference that with 1322 this dispersion was overdosed at 40%. The alteration of the DPTT/TMTD ratio to favor TMTD has the outcome that a 30 kg/sq cm SV can reliably be attained only with 140% of vulcanizing agents, and that this is at the expense of the tensile strength.

TABLE 4

INITIAL PROPERTIES OF VULCANIZATES OF STOCKS WITH DIPENTAMETHYLENE THIURAM TETRASULFIDE AS MAIN CROSSLINKING AGENT (II)

	1314			1315			1316		
DPTT	1.6			1.6			1.6		
TMTD	1.0			1.0			1.0		
MBT	1.0			—			0.5		
Hexa	—			1.0			0.5		
ZnO	3.0			3.0			3.0		
Cure time, hours, air, 100° C	T.S.	E/B	SV	T.S.	E/B	SV	T.S.	E/B	SV
1	241	596	32.9	357	865	15.9	326	668	30.2
2	241	543	42.4	411	738	29.7	350	624	38.6
3	212	524	46.8	417	717	35.3	280	564	44.7
4	227	496	48.9	347	647	35.9	—	—	—
1.5 (90° C)	—	—	—	—	—	—	332	765	21.3
3 (90° C)	—	—	—	—	—	—	378	663	33.5
4.5 (90° C)	—	—	—	—	—	—	368	618	39.9
6 (90° C)	—	—	—	—	—	—	357	608	43.4

TABLE 5

EFFECT OF OVER-DOSAGE OF THIURAM CROSSLINKERS

	1319			1322		
DPTT	0.8			1.12		
TMTD	1.0			1.4		
MBT	0.35			0.63		
Hexa	0.35			0.63		
ZnO	3.0			4.2		
Cure time, hours, air, 100° C	T.S.	E/B	SV	T.S.	E/B	SV
1	311	820	17.3	256	817	17.7
2	356	746	26.7	269	698	29.0
3	364	713	30.4	271	619	37.0
4	—	—	—	273	605	40.6
1.5 (90° C)	304	914	15.3	—	—	16.4
3 (90° C)	342	845	19.6	—	—	22.1
4 (90° C)	356	822	23.2	—	—	24.8
5 (90° C)	360	785	25.9	—	—	30.4

From a diagram plotting the stress values of vulcanizate 1316 as a function of the heating time at 90° C as well as 100° C the figures in Table 6 were to be found with in each case the same stress value; from this it follows that at 90° C we need 2.13 times the 100° C heating time to get the same stress value or degree of cure. The experiments which follow were planned to reduce this vulcanization-time factor. The aim was to achieve full cures at temperatures as low as 90° C in the shortest possible time. It was found that with increasing DPTT or with increasing proportion of DPTT in the combination DPTT/TMTD it is possible to lower the vulcanization-time factor.

The experiments surveyed in Table 7 show on the one hand the superiority of DPTT over TMTD as a main crosslinking agent (stocks 1324 and 1327 as compared with stocks 1325 and 1328) and on the other hand the fact that the combination DPTT/TMTD is considerably more active than the combination DPTT/TMTM (stocks 1323 and 1326 as compared with stocks 1324 and 1327). The advantage of shifting the DPTT/TMTD proportion to favor the DPTT is shown by the stress values and vulcanization-time factors of vulcanizates 1323 and 1326. In addition we can see that it is possible to get a proper full cure at 90° C. It is of interest to note the pronounced plateau in the stress value of vulcanizate 1326 and the tensile strength as compared with vulcanizate 1323.

THE DEGREE OF VULCANIZATION INDEX

In the course of the experiments it was found that the 300/300 value was worthless for assessing the vulcanization degree index, as is shown for instance

TABLE 6

EQUIVALENT VULCANIZATION TIMES AT 90° C AND 100° C FOR GIVEN STRESS VALUES OF VULCANIZATES FROM MIX 1316 (TABLE 4)

SV reached	at 90° C	at 100° C	90° C:100° C
34.7 kg/sq cm	in 197 min	in 90 min	2.19
38.6 kg/sq cm	in 250 min	in 120 min	2.08
42.0 kg/sq cm	in 320 min	in 150 min	2.13
Vulcanization time factor, 90° C:100° C averaging			2.13

TABLE 7

INITIAL PROPERTIES OF VULCANIZATES OF STOCKS WITH DIPENTAMETHYLENE-THIURAM TETRASULFIDE AND TMTD AS MAIN CROSSLINKING AGENTS AND TMTD AND TMTM AS SECOND ACCELERATORS (SECOND CROSSLINKING AGENTS)

	1323		1324		1325		1326		1327		1328	
DPTT	1.0		1.0		—		1.25		1.25		—	
TMTD	1.0		—		1.0		0.75		—		0.75	
TMTM	—		1.0		1.0		—		0.75		1.25	
MBT	0.67		0.67		0.67		0.67		0.67		0.67	
Hexa	0.33		0.33		0.33		0.33		0.33		0.33	
ZnO	3.0		3.0		3.0		3.0		3.0		3.0	
Cure time, hours, air, 100° C	T.S.	E/B	T.S.	E/B	T.S.	E/B	T.S.	E/B	T.S.	E/B	T.S.	E/B
1	351	821	265	704	109	1067	398	727	—	—	—	—
2	354	713	288	703	—	—	397	689	—	—	—	—
3	345	677	244	647	—	—	385	669	—	—	—	—
4	354	678	263	641	41	1105	404	675	—	—	—	—
1.5 (90° C)	347	830	272	718	139	1080	422	760	—	—	—	—
3 (90° C)	337	725	270	677	—	—	385	672	—	—	—	—
4.5 (90° C)	325	673	248	643	—	—	398	696	—	—	—	—
6 (90° C)	353	676	266	667	69	1175	381	668	—	—	—	—
	SV		SV		SV		SV		SV		SV	
1	20.7		21.8		8.9		29.2		25.0		10.8	
2	27.6		24.1		7.0		31.5		27.4		—	
3	32.5		27.6		5.5		33.3		30.1		—	
4	33.2		26.9		4.9		35.3		31.3		5.5	
1.5 (90° C)	19.1		20.9		9.3		28.0		23.5		12.7	
3 (90° C)	27.0		24.1		8.9		31.7		27.7		—	
4.5 (90° C)	31.5		25.0		7.0		34.2		28.8		—	
6 (90° C)	34.1		26.9		6.6		35.9		31.4		8.4	
Vulcanization-time factor	1.65		2.03		—		1.48		1.73		—	

TABLE 8

STRESS AND 300/300 VALUES OF VULCANIZATES OF STOCKS WITH DIPENTAMETHYLENETHIURAM TETRASULFIDES AND TMTD AS MAIN CROSSLINKING AGENTS

	1308	1309	1310	1311	1312	1313
DPTT	1.5	1.0	1.0	—	—	—
TMTD	—	1.0	1.0	2.0	2.0	2.0
MBT	1.5	1.0	1.0	1.0	1.0	—
Hexa	—	—	—	1.0	—	1.0
Diethylamine	—	—	0.5	—	—	—
ZnO	3.0	3.0	3.0	3.0	3.0	3.0
Cure time, hours, air, 100° C	SV	SV	SV	SV	SV	SV
1	26.8	18.4	18.4	7.6	8.1	7.8
2	29.1	27.5	28.5	6.2	5.6	6.2
3	30.1	31.4	32.8	4.9	4.2	6.0
4	30.6	33.7	33.5	4.5	3.9	6.0
	300/300	300/300	300/300	300/300	300/300	300/300
1	2.18	2.24	2.24	2.19	2.19	2.11
2	2.17	2.11	2.02	1.88	1.82	1.69
3	2.05	1.97	1.98	1.68	1.80	1.54
4	1.93	2.01	1.97	1.75	1.72	1.47

TABLE 9

VALUES FROM THE STRESS/STRAIN/RETRACTION DIAGRAM OF TWO VULCANIZATES WITH THE SAME 300/300 VALUE

Elongation, %	1326 Cured 1.5 h at 90° C	1328 Cured 4.0 h at 100° C
100	9.05	4.3
200	13.7	4.5
300	18.6	4.8
400	28.7	5.85
300 retraction	8.95	2.3
300/300 value	2.08	2.08

by the data in Table 8. According to this the 300/300 values of vulcanizates 1311 to 1313 are better than those of vulcanizates 1308 to 1310, while nevertheless 1311 to 1313 with TMTD as main crosslinking agent were regarded as

TABLE 10

DEGREE OF VULCANIZATION INDEXES OF TWO VULCANIZATES WITH EQUAL 300/300 VALUE, AS WELL AS OF OTHER EXPERIMENTAL VULCANIZATES

	1326 Cured 1.5 h at 90° C	1328 Cured 4 h at 100° C
$300_D/300_E$[1]	2.08	2.08
$300_D/100_D$	2.05	1.11
$300_E/100_D$	0.99	0.48
$300_D/100_D + 300_E/100_D$	3.04	1.60
$300_D/100_D \cdot 300_E/100_D$	2.03	0.55

Vulcanizate No.	1326	1327	1328	1328	1328	1328
Cure time, hours	1.5	1.5	1.5	6	1	4
Cure temperature, ° C	90	90	90	90	100	100
Stress value (400%), kg/sq cm	28.0	23.5	12.7	8.4	10.8	5.5
Vulcanization degree index calculated						
as sum	3.04	2.87	2.06	1.88	1.89	1.60
as product	2.03	1.78	0.79	0.74	0.70	0.55

[1] D = extent of elongation, E = extent of retraction.

markedly undercured. If we compare the data from the stress/strain curve of vulcanizates 1326 and 1328 in Table 9 with each other, we see the worthlessness of the 300/300 value. If however we relate the 100% value both to the 300%

TABLE 11

STRESS VALUES AND VULCANIZATION DEGREE INDEXES OF VULCANIZATES OF STAGE-HEATED STOCK 1326

Cure time, hours, 100° C	Stress value	Vulcanization degree index
1	34.6	2.12
2	37.8	2.40
3	38.8	2.54
4	41.8	2.49
1.5 90° C	31.2	1.92
3 90° C	37.4	2.22
4.5 90° C	39.0	2.28
6 90° C	40.0	2.58
5 85° C	39.6	2.22

Vulcanization-time factor 90°:100° C = 1.53.

TABLE 12

BASIC FORMULAS AND PROPERTIES OF TWO VULCANIZATES SUBJECTED TO AN EXTENDED HEAT AGING

	Thread stock 1335	Thread stock 2225
Colloidal sulfur 85%	—	1.50
Zinc ethylphenyldithiocarbamate	—	1.00
DPTT	1.50	—
TMTD	0.75	—
MBT	0.67	0.15
Hexa	0.33	—
ZnO	3.00	2.75
$ZnO \cdot H_2O$	—	0.40
DNP	—	0.50
Titanium dioxide	4.50	4.50
Cured 3 hours at 85° C, in air		
T.S., kg/sq cm	430	427
E/B, %	710	674
SV, 400%, kg/sq cm	34.1	45.7

value of the extent of elongation and also to the 300% value of the extent of retraction, for instance by division, and combine the two values, as may be effected either by addition or multiplication, we get a value which with increasing magnitude characterizes a steep rise in the stress value on elongation

TABLE 13

TIME (DAYS) NECESSARY FOR % LOSS IN TENSILE PRODUCT AT AGING TEMPERATURES OF 70°, 80°, 90° AND 100° C

Aging temperature, ° C	5%		10%		15%		20%		25%	
	1335	2225	1335	2225	1335	2225	1335	2225	1335	2225
70	9.5	0.7	29.0	1.0	—	1.3	—	1.7	—	2.1
80	9.1	1.1	9.7	1.95	11.0	2.7	—	3.4	—	4.0
90	1.1	0.25	2.05	0.45	3.2	0.65	6.05	0.85	—	1.1
100	0.2	0.1	0.28	0.2	0.5	0.3	0.83	0.43	1.45	0.55
for 2225 = 1										
70	13.6	1.0	29.0	1.0	—	—	—	—	—	—
80	8.3	1.0	5.0	1.0	4.1	1.0	—	—	—	—
90	4.4	1.0	4.6	1.0	4.9	1.0	7.1	1.0	—	—
100	2.0	1.0	1.4	1.0	1.7	1.0	1.9	1.0	2.6	1.0

and at the same time a small hysteresis loop. We get such calculations in lines 4 and 5 in Table 10. Multiplication is preferable to addition, because as Table 10 shows it gives differentiated values. It may be seen that the heating stages of the markedly undercured vulcanizates 1328 have their vulcanization

TABLE 14

TIME (DAYS) NECESSARY FOR % LOSS IN TENSILE STRENGTH AT AGING TEMPERATURES OF 70°, 80°, 90° AND 100° C

Aging temperature, ° C	5%		10%		15%		20%		25%	
	1335	2225	1335	2225	1335	2225	1335	2225	1335	2225
70	40.5	6.8	—	10.5	—	13.5	—	16.6	—	—
80	10.25	1.0	—	1.9	—	2.15	—	3.0	—	—
90	2.25	0.33	—	0.7	—	1.25	—	1.9	—	—
100	0.38	0.2	0.88	0.4	1.75	0.58	2.85	0.8	—	—

TABLE 15

TIME (DAYS) NECESSARY FOR 5, 10, 15, 20 AND 25% LOSS IN T.S. OR IN TENSILE PRODUCT AT 20° C

	T.S.		Tensile product	
Loss, %	1335	2225	1335	2225
5	3,500,000	150	13,500,000	10,500
10	—	350	—	—
15	—	470	—	—
20	—	880	—	—
25	—	1800	—	—

degree indexes well below 1, while for the well-cured vulcanizates 1326 and 1327 we get values round about 2.

The stress values of the stage-heated vulcanizates 1326 were determined afresh 16 days after cure, and from the data the vulcanization degree indexes quoted in Table 11 were calculated. In the later investigations we aimed at as high as possible a vulcanization degree index with short heating times and low heating temperatures.

TABLE 16

INITIAL PROPERTIES OF THIURAM VULCANIZATES WITH OPTIONAL AND COMBINED ADDITION OF SiO_2 AND DDA ANTIAGER

	1353	1354	1355	1356
TiO_2	4.5	4.5	3.0	3.0
SiO_2	—	—	3.0	3.0
DDA	—	1.8	—	1.8
Cured 3 hours at 90° C				
T.S., kg/sq cm	400	388	398	325
E/B, %	670	658	696	632
SV, 400%, kg/sq cm	36.3	33.0	34.7	34.3

Aging tests with extrapolation to room temperature.—When we had reached a certain degree of finality in this development, we carried out an extensive investigation of the aging behavior of a vulcanizate according to formula 1326 in comparison to one of the classical sulfur formulas; accelerated aging was carried out in stages at four temperatures, 70°, 80°, 90° and 100° C. The two specimens were based on the formulas given in Table 12.

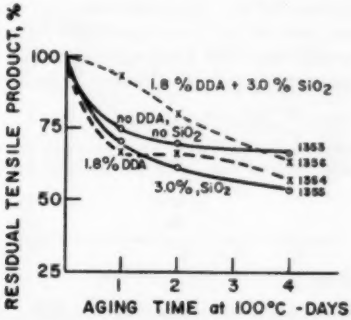

FIG. 11.—Residual tensile product of thiuram vulcanizates aged in stages at 100° C (Table 16).

TABLE 17

INITIAL PROPERTIES OF THIURAM VULCANIZATES WITH INCREASING ADDITIONS OF SiO_2

	1380	1376	1377
TiO_2	4.5	4.0	3.5
SiO_2	—	2.0	4.0
Cured 3 hours at 90° C			
T.S., kg/sq cm	437	386	373
E/B, %	682	680	689
SV, 400%, kg/sq cm	34.1	32.8	37.7

In Table 13 we collate the times which were necessary for the tensile product at a given aging temperature to fall by a given percentage. In the lower part of the table we take the values for 2225 the sulfur vulcanizate as being equal to 1, for reference. It means for instance that the sulfur vulcanizate at 80° loses 10% of its strength in 1.95 days, but that the thiuram vulcanizate takes 9.7 days to lose this much, i.e., five times the aging period. Table 14 with the

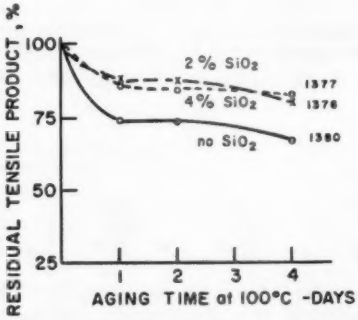

FIG. 12.—Residual tensile strength of thiuram vulcanizates with increasing additions of SiO_2, aged in stages at 100° C (with reference to Table 17).

corresponding values for tensile strength could be compiled only to an incomplete extent, since with the thiuram vulcanizate no losses above 10% were recorded at 70°, 80° or even 90° C. It is seen that the time differences at lower aging temperatures are greater thus extrapolation to room temperature was suggested. An extrapolation of this kind was carried out first by van Raamsdonk[4]. He found a linear relationship between the logarithm of the aging time

TABLE 18

INITIAL PROPERTIES OF THIURAM VULCANIATES WITH INCREASING ADDITIONS OF SiO_2 ($TiO_2 + SiO_2 = 4.5\%$)

	1383	1384	1385
TiO_2	4.5	2.5	0.5
SiO_2	—	2.0	4.0
Cured 3 hours at 90° C			
T.S., kg/sq cm	358	417	352
E/B, %	653	694	645
SV, 400%, kg/sq cm	37.0	37.5	39.4

TABLE 19

INITIAL PROPERTIES OF THIURAM VULCANIZATES WITH MBT OR MBTZN AS ACTIVATOR

	1422	1426	1430	1465	1466
DPTT	1.25	1.25	1.25	1.25	1.25
TMTD	0.75	0.75	0.75	0.75	0.75
MBT	1.00	—	0.50	1.00	—
MBTZn	—	1.00	0.50	—	1.00
ZnO	3.00	3.00	3.00	4.00	4.00
TiO_2	3.50	3.50	3.50	4.00	4.00
SiO_2	1.00	1.00	1.00	1.00	1.00
Cured 3 hours at 90° C					
T.S., kg/sq cm	438	467	410	448	538
E/B, %	710	754	694	729	811
Tens. prod. $\left(\frac{1}{1000}\right)$	311	352	285	327	436
SV, kg/sq cm	31.6	33.3	34.3	28.3	30.8

(the time necessary for a given loss in strength) and the reciprocal of the absolute temperature, so that it became possible to extrapolate to room temperature. Extrapolation to 20° C gave the values shown in Table 15. While according to these the sulfur vulcanizate 2225 loses 5% in tensile strength in 150 days (5 months) at 20° C in the dark (for the specimens were aged with light excluded), the thiuram vulcanizate 1335 requires for this the enormous time of 3,500,000 days (10,000 years). For the tensile product the times are 29 and 37,000 years respectively. The experimental data obtained at 70° C could not be taken into consideration here, as they came right outside the picture. Even if the times resulting from extrapolation appear incredible, they serve as a comparison to show the exceptional differences in the rates of aging in the two specimens—a confirmation that the nature of the vulcanization system has a more decisive influence upon aging than has the presence of an age resistor.

On the effect of high-activity silica.—The following experiments were intended to show whether the addition of high-activity silica to sulfur-free thiuram stocks would give a further increase in the aging resistance. Figure 11,

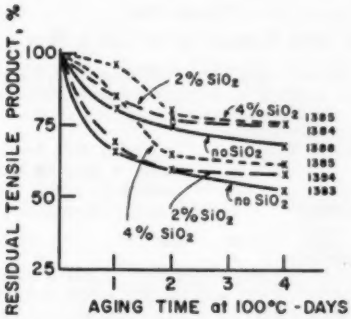

FIG. 13.—Residual tensile strength (upper bundle of curves) and residual tensile product (lower bundle of curves) of thiuram vulcanizates with increasing amount of SiO_2 and reduced addition of TiO_2 (SiO_2 + TiO_2 = 4.5%) (with reference to Table 18).

TABLE 20

INITIAL PROPERTIES OF A THIURAM VULCANIZATE WITH MBTZN AS ACTIVATOR (STOCK 1426) HEATED IN STAGES AT 87 TO 88° C

Cure time, h	SV	Vulc. degree index	T.S.	E/B	Tensile product
3	31.9	1.76	357	648	231,000
4	38.2	1.83	362	666	241,000
5	36.0	1.98	341	609	207,000
6	35.3	1.97	346	606	210,000
7	37.0	2.03	358	610	218,000
8	38.2	2.12	380	612	232,000
9	37.0	2.23	334	600	200,000
14	41.6	2.33	353	587	207,000
16	43.7	2.34	358	588	211,000
18	43.0	2.29	355	607	215,000
21	44.0	2.41	341	588	200,000
24	43.8	2.41	365	571	208,000

referring to the vulcanizates in Table 16, with optional addition of 3% Siflox silica and 1.8% DDA antiager, shows that neither the specimen with silica nor with the antiager showed better aging behavior than the reference sample, but that vulcanizate 1356, which contains both antiager and silica, showed a distinctly retarded rate of aging at least up to an aging time of 4 days at 100° C. A similar effect had already been observed in sulfur-vulcanized latex specimens[5].

The experiments covered by Table 17 gave clearer results. Figure 12 shows that the addition of as little as 2% silica gives an increase in the aging resistance. In order to exclude the filler effect of the silica, in the experiments shown in Table 18 we reduce the amount of titanium dioxide in proportion as we increased the amount of silica. We see, whether from the curves in Figure 13 for tensile strength (above) or from those of the tensile product (below), that a progressive replacement of titanium dioxide by silica gives a distinct improvement in aging.

Improvement of the basic formula by alteration of certain activators.—On finding, in the course of further experiments to improve the basic activator hexa and use instead the same amount of MBT, we examined the effectiveness of replacing MBT by its zinc salt, MBTZn. The data in Table 19 show that by this change we get higher tensile strength, elongation at break and stress

TABLE 20A

STOCKS WITH REFERENCE TO THE ACTIVE SULFUR

$(CH_2)_5N-\underset{\underset{S}{\|}}{C}-S-S-S-S-\underset{\underset{S}{\|}}{C}-N(CH_2)_5$ contains 50% by weight of sulfur, of this only half is labile, i.e. 25% active sulfur

Dipentamethylenethiuram tetrasulfide

$(CH_3)_2N-\underset{\underset{S}{\|}}{C}-S-S-\underset{\underset{S}{\|}}{C}-N(CH_3)_2$ contains 53% by weight of sulfur, of this only a quarter is labile, i.e. 13% active sulfur

Tetramethylthiuramdisulfide

	1440	1441	1442
Dipentamethylene thiuram tetrasulfide (25% S*)	1.875 = 0.470 S*	1.250 = 0.313 S*	1.250 = 0.313 S*
TMTD (13% S*)	1.125 = 0.150 S*	0.750 = 0.100 S*	0.750 = 0.100 S*
ZnO	3.00	6.50	3.00
Colloidal sulfur, 85%	—	—	0.250 = 0.212 S*
	0.620 S*	0.413 S*	0.625 S*

TABLE 21

EFFECT OF THE DIPENTAMETHYLENETHIURAM TETRASULFIDE/TMTD RATIO UPON THE PROPERTIES OF THE VULCANIZATES

	1501	1502	1503
DPTT	1.5	1.5	1.25
TMTD	0.5	0.5	0.75
MBTZn	1.0	1.0	—
MBT	—	—	0.675
Hexa	—	—	0.325
ZnO	3.5	3.5	3.5
$ZnO \cdot H_2O$	0.5	0.5	—
TiO_2	3.5	3.5	4.0
SiO_2	1.0	—	—
Cured 3 hours at 90° C			
T.S., kg/sq cm	502	505	405
E/B, %	784	771	712
Tens. Prod. $\left(\frac{1}{1000}\right)$	394	389	288
SV, kg/sq cm	30.6	29.7	25.2

values; in addition, as the figures for the stage heating of such a vulcanizate in Table 20 show, we get in this way a considerable degree of independence of the stress value of the heating time, and even the tensile strength is hardly endangered by overvulcanization.

The "chain of pearls" effect.—On the specimens so far there had from time to time been an effect which had been likened to a 'chain of pearls'. This refers to randomly occurring points of constriction on the slow retraction of thread-type specimens, which had just previously been stretched to close on breaking point. This effect occurs during retraction preferentially between 200% and 100% elongation, disappearing again completely below 100% elongation. As the phenomenon was not observed on any of the specimens which were aged for only 24 h at 100° C, it was suggested that the reason might be inadequate cure. Surprisingly the phenomenon could not be eliminated by the addition of elemental sulfur. With the experiments covered by Table 20a (stocks 1440 to 1442) we raised the usual amount of 1.25% DPTT + 0.75% TMTD by 50% in the first stock, so that it contained a total of 0.62% of so-called active sulfur, (if we take the amounts of labile sulfur from

TABLE 22

BASIC FORMULAS OF TWO VULCANIZATES TESTED FOR RATE OF AGING BY RELAXATION METHOD

	Thread 1507	Thread 2225
Colloidal sulfur, 85%	—	1.50
Zinc ethylphenyl dithiocarbamate	—	1.00
Dipentamethylenethiuram tetrasulfide	1.50	—
TMTD	0.50	—
MTZ	1.00	—
MBT	—	0.15
ZnO	3.50	2.75
$ZnO \cdot H_2O$	—	0.40
ARW	—	0.50
TiO_2	4.00	4.50
SiO_2	0.50	—

TABLE 23

RELAXATION HALF-VALUE TIMES OF A THIURAM AND A SULFUR VULCANIZATE

Temperature ° C	Thiuram specimen 1507 80% elongation	Sulfur specimen 2225	
		80% elong.	175% elong.
100	—	27.2	—
110	—	9.8	9.8
120	17.5	2.9	3.45
130	6.33	0.93	0.75
140	—	0.35	0.33
142	1.74	—	—
150	0.85	0.13	0.13
160	0.33	—	—

DPTT, at 25%, and from TMTD, at 13%, as being correct). In the second stock the amount of zinc oxide was doubled, and in the third we added so much colloidal sulfur that altogether we again had 0.62% of active sulfur. The vulcanizate from the first-named stock (1440) was found not to have the 'chain of pearls' effect, the same was the case for the second (1441), while that of the third (1442) had the effect after as well as before aging and in addition had a lower stress value. We might deduce from this that in thiuram vulcanizates not only the labile sulfur causes crosslinking, but that in addition fragments of the thiuram molecules participate effectively in the crosslinking. The fact that crosslinking by thiuram compounds takes place only in the presence of zinc oxide is already known and it becomes understandable why larger amounts of zinc oxide are necessary in latex stocks than in solid rubber stocks when we consider that as a result of the presence of 50% of water the concentrations in the latex stocks are only half as high.

Further experiments, to show which of the two thiuram compounds called for the higher dosage to avoid the chain of pearls effect showed that a higher dosage of DPTT has a positive effect, while TMTD is negative, but on the other hand too great a reduction in the TMTD also has adverse consequences. Finally the basic formula was corrected to alter the DPTT/TMTD addition to the molar ratio of 2:1 and reduce the zinc oxide to 4 or 5%. In addition a total accelerator content of 3% was found to be quite sufficient, but the curing temperature of 90° C could not be lowered. Table 21 gives data for 3 vulcanizates (1501 to 1503). The two first are based on the formula with the molar ratio of 2/1 for DPTT/TMTD using MBTZn, getting tensile strength figures of over 500 kg/sq cm, while the tensile strength of the third vulcanizate, based

TABLE 24

RESIDUAL TENSILE STRENGTH H (% OF INITIAL FIGURE) OF AGED THIURAM VULCANIZATES WITH OPTIONAL AND COMBINED ADDITION OF ANTIAGERS DDA AND ARW

	1508	1509	1510	1511	1512	1513
DDA	—	1.0	—	1.0	—	1.0
ARW	—	—	0.5	0.5	1.0	1.0
TiO_2	4.0	4.0	3.5	3.5	3.0	3.0
Residual T.S., %						
Aged 3 days 100° C	80	68	81	67	78	71
Aged 6 days 90° C	79	74	87	70	67	80
Aged 12 days 80° C	83	71	72	74	83	84
Average	81	71	80	70	76	78

TABLE 25

RESIDUAL TENSILE STRENGTH AND ELONGATION AT BREAK OF AGED THIURAM VULCANIZATES WITH AND WITHOUT THE ANTIAGER MBIZN (I)

	1529		1530	
DPTT	1.45		1.45	
TMTD	0.45		0.45	
MBTZn	1.10		0.55	
MBIZn	—		0.55	
Residual T.S. and E/B, %	T.S.	E/B	T.S.	E/B
Aged 1 day at 100° C	81	81	85	86
Aged 3 days at 100° C	68	74	90	87
Aged 7 days at 100° C	60	75	79	80

on the old formula and using MBT + hexa was only slightly above 400 kg/sq cm, and the elongation at break was lower, although the stress value was also lower.

Aging experiments by the relaxation method.—The Kautschukinstitut of the Technische Hochschule, Hanover, kindly investigated the rate of aging of the

TABLE 26

RESIDUAL TENSILE STRENGTH AND ELONGATION AT BREAK OF AGED THIURAM VULCANIZATES WITH AND WITHOUT MBIZN ANTIAGER (II)

	1537		1538	
MBIZn	—		0.5	
Residual T.S. and E/B, %	T.S.	E/B	T.S.	E/B
Aged 1 day at 100° C	76	79	90	87
Aged 2 days at 100° C	78	77	88	87
Aged 7 days at 100° C	71	75	73	84

specimens based on the vulcanization systems under dicussion, using the relaxation method developed by Hillmer and Scheele[6]. The composition of the thread shaped specimens (1507 and 2225) is shown in Table 22. W. Scheele wrote with reference to the investigations that it had not been found possible to get experimental conditions under which the stress relaxation would proceed

TABLE 27

INITIAL PROPERTIES OF SULFUR AND THIURAM VULCANIZATES WITH AND WITHOUT AGE RESISTOR

	1545	1546	1548	1549
Colloidal sulfur, 88 to 90%	1.5	1.5	—	—
Zinc ethylphenyldithiocarbamate	1.0	1.0	—	—
MBT	0.15	0.15	—	—
DPTT	—	—	1.5	1.5
TMTD	—	—	0.5	0.5
MBTZn	—	—	1.0	0.75
ZnO	2.75	2.75	4.0	4.0
$ZnO \cdot H_2O$	0.4	0.4	—	—
TiO_2	6.0	5.5	4.0	4.0
SiO_2	—	—	0.5	0.5
Antiager BKF	—	0.5	—	—
Antiager MBIZn	—	—	—	0.5
Cured 3 hours 90° C				
T.S., kg/sq cm	432	404	400	404
E/B, %	688	661	670	656
SV, 400%, kg/sq cm	40.4	37.9	41.0	40.0

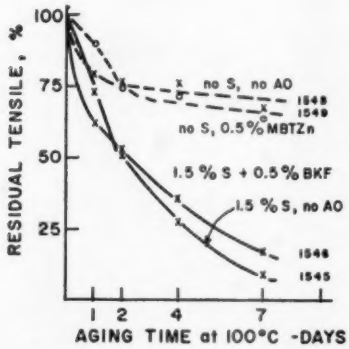

FIG. 17.—Residual tensile strength of two sulfur and thiuram vulcanizates, with and without antioxidant (AO), aged in stages at 100° C (with reference to Table 27).

as a zero order reaction. This would be very difficult with threads, which like thread stock 1507 would be essentially thiuram vulcanizates, because they are exceptionally aging-resistant. But also thread stock 2225 could not be measured according to zero order, which may be connected with the fact that this vulcanizate contains DNP antiager. For this reason the half-value times (the times for the relative stress to die away by 50%) were taken as a basis in both cases. The experiments were carried out in oxygen and in the temperature range between 100° and 160° C. Table 23 compared the relaxation half-value times for the two thread stocks and shows that the aging rates differ by roughly a factor of 6.

On the effect of age resistors.—In order to test whether a reduction in the rate of aging of thiuram vulcanizates is possible by means of the addition of age resistors, we added combinations of the antiagers DDA and ARW in a further series of experiments. The aging was continuous, for 3 days at 100°, 6 days at 90° and 12 days at 80° C. The results are shown in Table 24, from which we see that the antiager additions bring no improvement in the aging behavior,

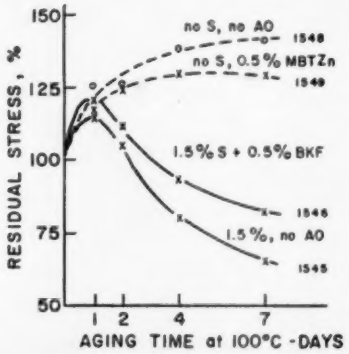

FIG. 18.—Residual stress values of two sulfur and thiuram vulcanizates with and without antioxidant (AO), aged in stages at 100° C (with reference to Table 27).

TABLE 28

RESIDUAL TENSILE STRENGTH AND STRESS VALUE OF AGED SULFUR AND THIURAM VULCANIZATES WITH AND WITHOUT AGE RESISTOR, UNAGED = 100

	1573		1574		1575		1576		1577	
Colloidal sulfur	1.5		1.5		1.5		—		—	
MBIZn	—		1.0		—		—		1.0	
BKF	—		—		1.0		—		—	
SiO_2	2.0		2.0		2.0		2.0		2.0	
Aged	T.S.	SV	T.S.	SV	T.S.	SV	T.S.	SV	T.S.	SV
28 days 70° C	71	128	67	153	89	143	86	150	83	144
1 day 100° C	73	109	79	121	75	109	87	126	87	123
2 days 100° C	53	99	55	138	63	117	84	138	76	131
4 days 100° C	17	73	50	126	34	101	75	136	77	141
7 days 100° C	3	63	26	107	18	98	66	147	72	138
14 days 100° C	0	—	3	—	3	—	32	—	55	138

whether we use ARW or DDA or a combination of them. The amount of the age resistor likewise seems to have no influence. This is further confirmation of the investigations and conclusions of Ossefort, Shaw and Bergström[7] according to whom the choice of a "good" vulcanization system is more important for the aging resistance than the employment of age resistors.

On the effect of the zinc salt of mercaptobenzimidazole.—After the negative result with the two antiagers referred to, experiments were carried out with the zinc salt of mercaptobenzimidazole, MBIZn, whose specific effect in thiuram stocks is well known. In a preliminary experiment we obtained the aging figures shown in Table 25. The results encouraged us to further experiment along these lines. Table 26 likewise shows that even as little as 0.5% of MBIZn has a distinct effect. We carried out a series of experiments with two specimens crosslinked with sulfur and two with thiuram compounds, and of these the one specimen with no antiager, the other with BKF or MBIZn antiager, which were aged in stages for up to 7 days at 100° C. It is noteworthy that, as we see from Table 27, all four vulcanizates, which were heated

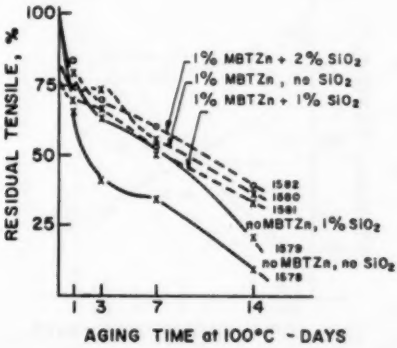

FIG. 21.—Residual tensile strength of thiuram vulcanizates with optional or combined addition of MBIZn and SiO_2, aged by stages at 100° C. Note: MBTZn on this figure should read MBIZn.

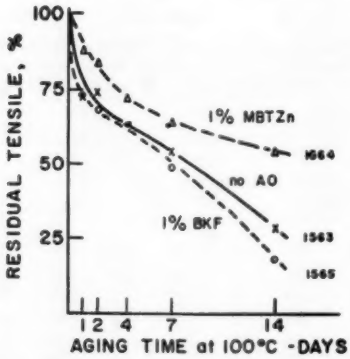

FIG. 22.—Residual tensile strength of thiuram vulcanizates with and without antiager (AO) in the absence of SiO_2 aged in stages at 100° C (with reference to Table 29). Note: MBTZn on this figure should read MBIZn.

under the same conditions of temperature and time, have likewise the same initial properties. Figure 17 immediately shows the pronounced difference between the two types of vulcanizate: whereas with the sulfur vulcanizates (1545 and 1546) the tensile strength falls to below 20% of the initial value after 7 days' aging, the thiuram vulcanizates (1548 and 1549) still retain more than 60% of their tensile strength after the same period. Another typical feature is the change in stress values, Figure 18 shows that with the sulfur specimens the stress value increases at first, then decreasing continuously as the aging time increases, while the thiuram specimens increase their stress value continuously up to the end of the aging time. Table 28 gives the results of a further similar series of experiments in which MBIZn was used in one of the sulfur stocks. The aging time at 100° C was extended to 14 days. In parallel with this there was an accelerated aging over a period of 28 days at 70° C. We see from Table 28 that at this low temperature of aging MBIZn has no effect whatever, whether in the sulfur-crosslinked specimens (1573 to 1575)

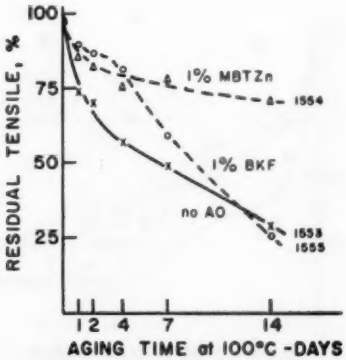

FIG. 23.—Residual tensile strength of thiuram vulcanizates with and withou tantiager (AO) with 1% SiO_2, aged in stages at 100° C (with reference to Table 29). Note: MBTZn on this figure should read MBIZn.

TABLE 29

PATTERN OF FORMULAS OF FOUR SERIES OF EXPERIMENTS WITH THIURAM VULCANIZATES WITH INCREASING AMOUNT OF SiO_2 AND OPTIONAL ADDITIONS OF MBIZN AND BKF

Mix No.	SiO_2 (%)	TiO_2 (%)	MBIZn (%)	BKF (%)
1563	0	4	0	0
1564	0	4	1	0
1565	0	4	0	1
1553	1	3	0	0
1554	1	3	1	0
1555	1	3	0	1
1560	2	2	0	0
1561	2	2	1	0
1562	2	2	0	1
1566	4	0	0	0
1567	4	0	1	0
1568	4	0	0	1

or in those crosslinked by the thiuram compounds (1576 and 1577), while at 100° C the reduction in the rate of aging is all the more evident—a confirmation of the well-known suitability of MBIZn as an antiager for heat-resistant thiuram stocks with sulfur-free vulcanization. Equally impressive is the picture of the alteration in the stress values, at 100° C.

The effect of high activity silica in the presence of the zinc salt of mercaptobenzimidazole.—In order to show whether comparatively small additions of high-activity silica to thiuram stocks containing MBIZn give a further increase in the aging resistance of the vulcanizates, we carried out a number of experiments with the following basic formula:

DPTT	1.5%
TMTD	0.5%
MBTZn	1%
ZnO	5%
$TiO_2 + SiO_2$	4%

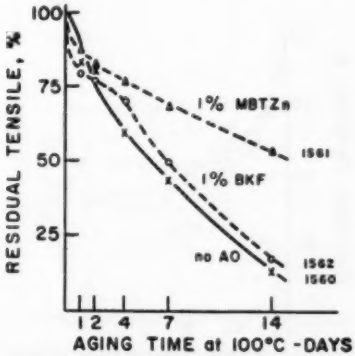

FIG. 24.—Residual tensile strength of thiuram vulcanizates with and without antiager (AO) with 2% SiO_2, aged in stages at 100° C (with reference to Table 29). Note: MBTZn on this figure should read MBIZn.

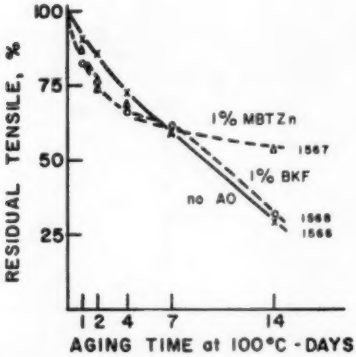

FIG. 25.—Residual tensile strength of thiuram vulcanizates with and without antiagar (AO) with 4% SiO_2, aged in stages at 100° C (with reference to Table 29). Note: MBTZn on this figure should read MBIZn.

Vulcanization was for three h at 90° C in air. In these experiments the aging time at 100° C was extended generally to 14 days, in order to get clear differentiation. Figure 21 shows the very marked effect of only 1% of silica in a MBIZn free stock according to the basic formula in question, but also shows that in the presence of MBIZn the corresponding interpretation is not possible.

Table 29 gives the pattern of the formulas for four sets of experiments with thiuram vulcanizates on the formula referred to. Figures 22, 23, 24 and 25 show that the vulcanizate with MBIZn has in every case the highest aging resistance and that there is no noticeable difference in the pattern of aging of the vulcanizates without antiager and with BKF. Figure 26 shows the drop in the tensile product with time for the specimens in Table 29 containing MBIZn and the surprisingly good result with the vulcanizate containing only 1% silica is evident. In connection with this it must be mentioned that in specimens using different batches of latex it was not only possible to get different initial properties, but also different rates of aging. The use of accelerators of different

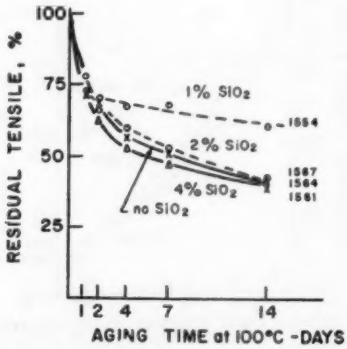

FIG. 26.—Residual tensile product of thiuram vulcanizates with 1% MBIZn in the presence of increasing amounts of SiO_2, aged in stages at 100° C (with reference to Table 29).

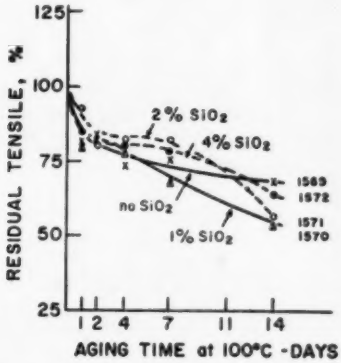

FIG. 27.—Residual tensile product of thiuram vulcanizates with 1% MBIZn in the presence of increasing amounts of SiO_2.

origin also has similar effects. Comparison based on Figure 26 is bound to lead to false conclusions, since the specimens in the last series of experiments came from different batches of latex, and in one case the TMTD used was Vulkacit Thiuram (Bayer), in the other Thiuram M (du Pont). Therefore the series of experiments corresponding to Figure 26 were repeated using one and the same latex batch and vulcanizing agents of the same firm. The result is shown in Figure 27. We see that up to an aging time of 4 days the specimens with silica behave better than that without, and that up to an aging time of 11 days the vulcanizates containing 2 and 4% of silica hold their own well against the silica-free vulcanizates. Figures 28 and 29 are also very informative; they show that with increasing silica content the degree of stiffness decreases, it being noticeable that with the MBIZn-containing vulcanizates as little as 1% silica reduces this stiffening considerably. A similar, if not so pronounced, picture is given in Figure 30, for a series of experiments repeated on the same latex batch.

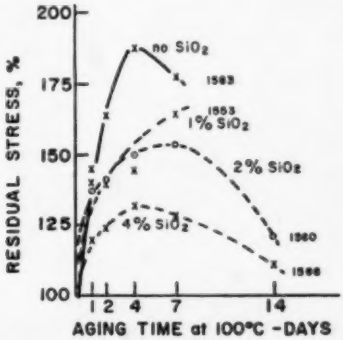

FIG. 28.—Residual stress values of thiuram vulcanizates without antiager in the presence of increasing amounts of SiO_2 (with reference to Table 29).

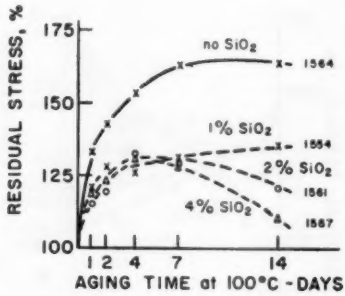

FIG. 29.—Residual stress values of thiuram vulcanizates with 1% MBIZn in the presence of increasing amounts of SiO_2 (with reference to Table 29).

In order to get a clear picture of the effect of a silica addition to stocks containing MBIZn, 6 completely similar series of experiments were carried out with 4 different stocks from different latex batches, namely with the above mentioned basic formula two stocks without MBIZn, the first without and the second with 3% silica, and then two stocks with 1% MBIZn with the first without and the second with 3% silica. Here again, as in the previous series of experiments, the TiO_2 amounts were reduced by the amount of SiO_2 added in each case, in order to rule out the 'filler effect'; the amount of $TiO_2 + SiO_2$ was 4% in every case, so that the silica-free stocks contained 4% titanium dioxide while those with 3% silica contained only 1%. The results of the six series of experiments confirm each other very clearly: 3% of silica noticeably improves the already outstanding age resistance of the thiuram vulcanizate containing MBIZn. The aging data for the last three series of experiments are averaged and collated in Table 30.

They show the effect of silica in slowing down the rate of aging, both in the absence and the presence of MBIZn, and it is noteworthy that even if the protective effect of the 1% MBIZn looked at on a long term basis is greater than that of 3% silica, silica itself is more effective in the initial stage of aging

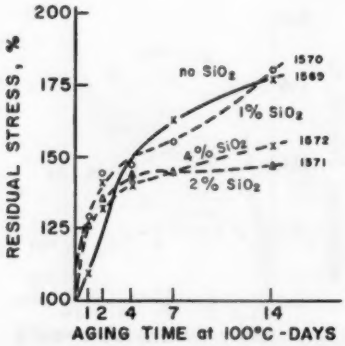

FIG. 30.—Residual stress values of thiuram vulcanizates with 1% MBIZn in the presence of increasing amounts of SiO_2, aged in stages at 100° C.

TABLE 30

AVERAGE VALUES OF THREE SERIES OF AGING EXPERIMENTS, 1612–1617, 1621–1624 AND 1637–1640

a) Residual tensile strength, %, of thiuram vulcanizates after aging for

7 days at 100° C

without MBIZn 42	without MBIZn, 3% SiO_2 58
1% MBIZn 64	1% MBIZn, 3% SiO_2 72

14 days at 100° C

without MBIZn 23	without MBIZn, 3% SiO_2 30
1% MBIZn 53	1% MBIZn, 3% SiO_2 59

b) Time in days necessary for 30, 40, 50, 60 and 70% loss in tensile product at an aging temperature of 100° C

Loss, %	30	40	50	60	70
without MBIZn without SiO_2	0.4	0.9	1.9	3.6	6.4
without MBIZn 3% SiO_2	2.1*	3.6*	5.3	8.2	(9.6)
1% MBIZn without SiO_2	1.0	2.2	6.0	13.8	—
1% MBIZn 3% SiO_2	1.7	5.8	11.8	(19.2)	—

c) Time in days necessary for 30, 40, 50, 60 and 70% loss in tensile strength at an aging temperature of 100° C

Loss, %	30	40	50	60	70
without MBIZn without SiO_2	1.2	2.5	4.4	7.8	11.3
without MBIZn 3% SiO_2	4.4*	6.6	9.1	11.6	(12.3)
1% MBIZn without SiO_2	3.7	9.5	16.2	—	—
1% MBIZn 3% SiO_2	8.0	13.4	(17.9)	—	—

than is the antiager MBIZn. This is shown by the asterisks in Table 30 which shows the averaged values of the three series of experiments.

REFERENCES

[1] Andresen, A., *Kautschuk u. Gummi* **11**, No. 9, WT 244-52 (1958).
[2] Jahrestagung, Arbeitsgemeinschaft Helle Verstärkerfüllstoffe für Kautschuk, Oct. 1958; *Kautschuk u. Gummi* **11**, WT 344-6 (1958).
[3] Willums, J., *Gummi Zeitung und Kautschuk, Gesamtausgabe, Kautschuk* **20**, 37–8 (1944).
[4] van Raamsdonk, G. W., Publication No. 295 of Rubber Stichting, Delft; in English.
[5] Andresen, A., *Kautschuk u. Gummi* **11**, WT 247 (1958).
[6] Hillmer, K.-H. and Scheele, W., *Kautschuk u. Gummi* **11**, WT 210-4 (1958); RUBBER CHEM. & TECHNOL. **32**, No. 3, 759–69 (1959).
[7] Ossefort, Z. T., Shaw, R. F. and Bergström, E. F., *Rubber World* **135**, 867–75 (1957); **136**, 65–73 (1957).

STABILIZATION OF NEOPRENE. I. PROTECTION OF LATEX FILM AGAINST DISCOLORATION BY LIGHT *

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INTRODUCTION

Neoprene vulcanizates tend to discolor when exposed to light. Pastels turn yellow and eventually brown if exposed long enough to rays from the sun or a sunlamp, even through glass. Products made from latex are more prone to darken than are the vulcanizates of dry mixes. The quality of neoprene products is not affected by discoloration per se, but for aesthetic reasons it is desirable to minimize color change.

Much research effort has been directed in the past toward improving the stability of neoprene vulcanizates to discoloration on exposure to light. Walter, Mantell and Gladding[7] reported that the presence of oxygen was essential for neoprene to discolor in light. Forman and Torrence[1] showed that nickel dibutyldithiocarbamate significantly inhibited discoloration but its green color and high pigmentation effect limited its use to mass toned articles. Walter[6] showed that *o*-benzylhydroxylamine had merit as a discoloration inhibitor for neoprene.

Thompson, Baker and Brownlow[4] and later Murray[2] have shown that certain unsaturated vegetable oils enhance significantly the ozone resistance of neoprene. Because both the discoloration of neoprene and attack by ozone are known to involve an oxidation phenomenon and may be indirectly related, and because vegetable oils are known to interfere with ozone attack, it was decided to study them as neoprene discoloration inhibitors during exposure to light.

PROCEDURE

Sample preparation.—Specimens used for most of the work reported herein were prepared by coating a 16 ounce rayon fabric with the neoprene latex compound to be studied. When other physical properties than color stability were desired films were prepared by coagulant dipping.

The fabric to be coated was placed on a glass plate and secured on the edges with masking tape. The latex compound was poured across the top edge of the fabric, and a Gardener knife was used to draw the compound down the length of the fabric. The knife clearance was set to give a coating thickness of 8 mils after drying. The coated fabric samples were dried at room temperature for 1 hour, then hung in an air oven at 100° C for 15 minutes to complete the drying.

Films were prepared on 2-inch diameter by 8-inch high glass tubes using the Anode dipping process[5]. A mixture of equal parts of acetone and methanol

* Contribution No. 181 from the Elastomer Chemicals Department presented before the Division of Rubber Chemistry, Louisville, Kentucky, April, 1961.

containing 10% each of calcium chloride and calcium nitrate was used as the coagulant. The wet coagulated films were leached for 2 hours in water at 40° C, then dried overnight at room temperature and 3 hours at 70° C in an air oven. The films were cured in an air oven as specified in the data that follows.

Test methods.—Color stability was determined by sunlamp exposure (ASTM D-925-55, Method B, Migration Stain 6b), indoors behind a window facing south in Delaware and Texas, and outdoors in Delaware. Stress-strain properties were determined by ASTM D-412-51. Heat aging was done in accordance with ASTM D-573-53. The brittleness temperature was determined by ASTM D-746-55. Ozone resistance was determined on ¼″ by 6″ strips of film from latex at 20% stress in an ozone concentration of 3 parts per million.

Materials.—The following commercial materials were used as compounding ingredients throughout this investigation:

Sodium dibutyldithiocarbamate—Tepidone, E. I. du Pont de Nemours & Co.
Tetraethylthiuram disulfide (TETD)—Thiuram E, E. I. du Pont de Nemours & Co.
"Hindered phenol"—Zalba Special, E. I. du Pont de Nemours & Co.
Raw linseed oil, Spencer Kellogg and Sons, Inc.
Olive oil, H. J. Baker and Bro.
Palm oil, Pacific Vegetable Oil Corp.
Raw tung oil, Merchant Products Corp.
Safflower oil, nonbreak, Pacific Vegetable Oil Corp.
Dibutyl tin dilauryl mercaptide—Thermolite 20, Metal and Thermit Corp.
Epoxy resins—Epon 828, Shell Chemical Co.; Paraplex G-62, Rohm & Haas Co.
Thiocarbanilide—Accelerator A-1, Monsanto Chemical Co.
Zinc dibutyldithiocarbamate—Butyl Zimate, R. T. Vanderbilt Co.
Polyalkyl phenol—Agerite Superlite, R. T. Vanderbilt Co.
Styrenated phenol—Wingstay S, Goodyear Tire & Rubber Co., Chemical Div.
2,2′-methylene-bis(4-methyl-6-*t*-butyl phenol)—Antioxidant 2246, Calco Div., American Cyanamid Co., Rubber Chemicals Dept.
2,2′-methylene-bis(4-ethyl-6-*t*-butyl phenol)—Antioxidant 425, Calco Div., American Cyanamid Co., Rubber Chemicals Dept.

RESULTS

Zinc oxide and antioxidant.—Zinc oxide and antioxidants are used in almost all neoprene compounds to provide adequate resistance to the deteriorating influences of heat and oxygen. Zinc oxide also is a curing agent and functions as an acid acceptor for the trace amounts of HCl released from neoprene during cure and aging. The effect of zinc oxide and antioxidant on the discoloration of neoprene latex films in light was studied first. Many very good antioxidants such as the amine types, themselves, seriously discolor elastomers when exposed to light. A nondiscoloring hindered phenol type, therefore, was used. Samples comparing Neoprene Latex 842A uncompounded, 842A with 5 parts of zinc oxide, and 842A with 2 parts of nondiscoloring antioxidant are shown in Figure 1 before and after exposure under a sunlamp for 12 and 24 hours. Surprisingly, in spite of its known stabilizing effect against oxygen, zinc oxide did not inhibit discoloration in light. The antioxidant did have a pronounced

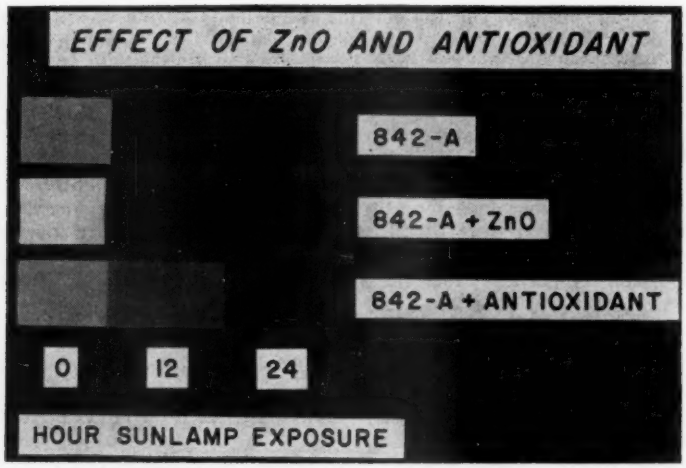


Fig. 1.

stabilizing effect, however. All subsequent studies, therefore, were made using compounds containing 2 parts of a hindered phenol type antioxidant.

The following base compound was used in subsequent studies:

Neoprene from latex	100
Hindered phenol type antioxidant	2
Zinc Oxide	10
Titanium Dioxide	20

The zinc oxide was included for curing and good oxidation resistance and the titanium dioxide for uniform original whiteness.

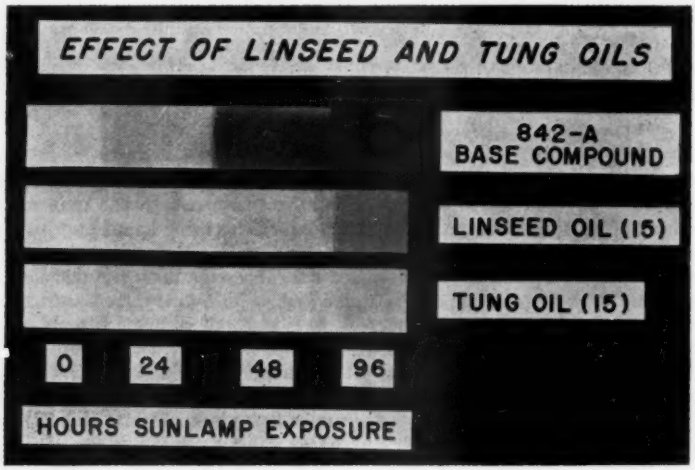


Fig. 2.

Linseed and tung oils.—Linseed and tung oils were studied first at the 15 part level in Neoprene Latex 842A using the base compound shown above. Samples of fabric coated with these compounds after exposure for 24, 48 and 96 hours under the sunlamp are shown in Figure 2. Both of the oils minimized discoloration markedly, tung more so than linseed oil. These oils, which are triglycerides of unsaturated fatty acids with three double bonds, tend to discolor themselves and this may have masked their full benefit as discoloration inhibitors in neoprene.

Degree of unsaturation.—To study the effect of the degree of unsaturation of the oil on discoloration of neoprene in light, a series of vegetable oils of increasing degree of unsaturation in the fatty acid radical was tried next. Palm oil, predominately palmitic acid triglyceride (unsaturated); olive oil, predominately oleic acid triglyceride (singularly unsaturated); safflower oil,

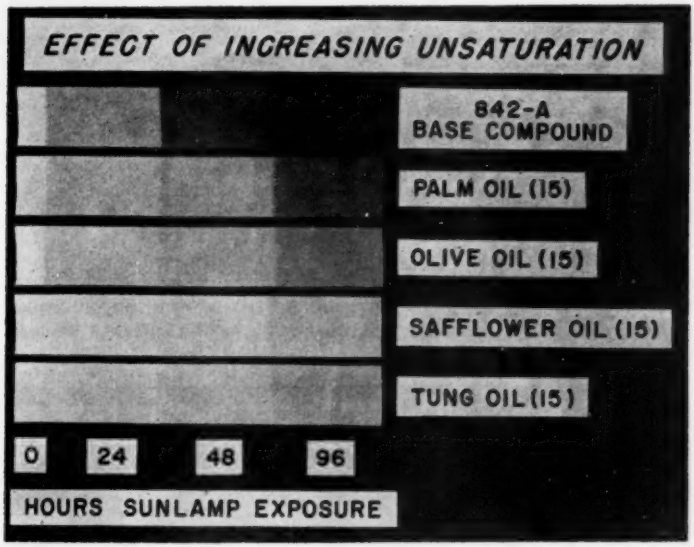


FIG. 3.

predominately linoleic acid triglyceride (doubly unsaturated); and tung oil, predominately eleostearic acid triglyceride (conjugated triply unsaturated), were added to a Neoprene Latex 842A compound in the amount of 15 parts. The effect of sunlamp exposure on these films before and after 24, 48 and 96 hours is shown in Figure 3. Each oil had some stabilizing influence, but stability increased with increasing unsaturation up to two double bonds (safflower oil). Tung oil was about equivalent to safflower oil, but showed no further improvement from the increased unsaturation. Because safflower oil is essentially odorless and readily available, it was selected for further investigation in preference to tung oil.

Amount of safflower oil.—The effect of the amount of safflower oil on the discoloration of Neoprene Latex 842A on exposure to light was studied next. Sunlamp exposures showing a control with no oil compared to samples with

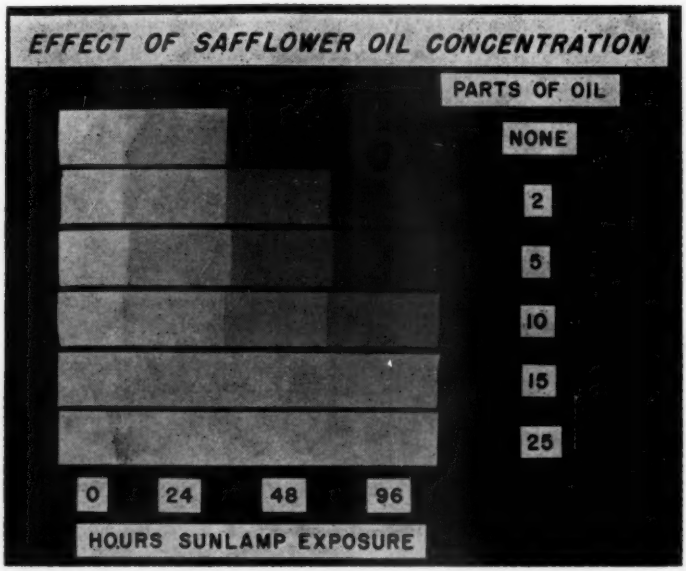


FIG. 4.

2, 5, 10, 15 and 25 parts of safflower oil are shown in Figure 4. Resistance to discoloration increased with increasing oil up to 15 parts beyond which no significant advantage was noted. A concentration of 15 parts therefore was used in further studies.

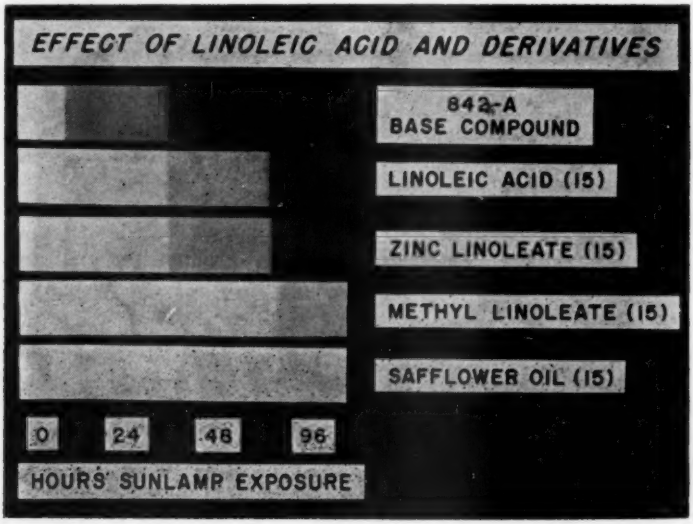


FIG. 5.

Linoleic acid and derivatives.—A study to determine the relative effect of the various structural components within the linoleic acid triglyceride molecule on discoloration in light was made next. Linoleic acid, its methyl ester and zinc salt were evaluated at the 15 part level in a Neoprene Latex 842A compound. The results after sunlamp exposure for 24, 48 and 96 hours compared to 842A samples containing 15 parts of safflower oil are shown in Figure 5. Note that methyl linoleate offered just slightly less protection than did safflower oil. Linoleic acid and zinc linoleate had some activity, but it was of a low order. Apparently the ester linkage as well as the linoleate radical has a considerable influence in inhibiting discoloration of the neoprene compounds in light.

Effect of antioxidants.—Several antioxidants were compared next in the presence of 15 parts of safflower oil for their effect on the discoloration of

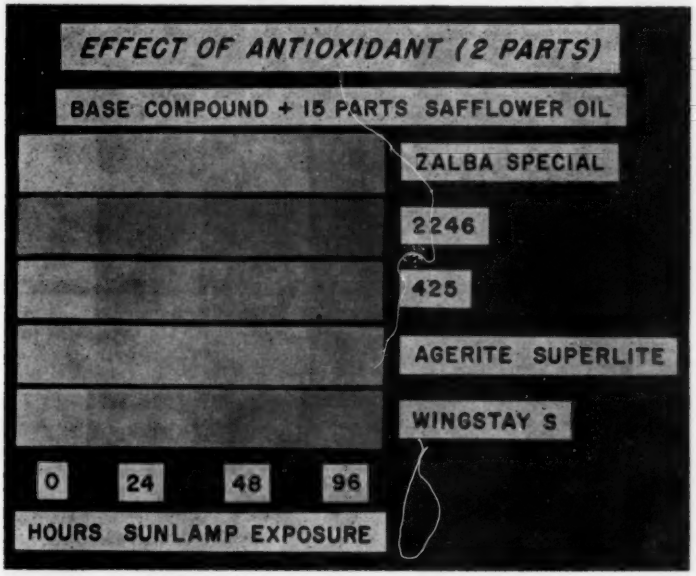


FIG. 6.

Neoprene Latex 842A compounds. 2,2′-Methylene-bis(4-methyl-6-*t*-butyl phenol), 2,2′-methylene-bis (4-ethyl-6-*t*-butyl phenol), a polyalkyl phenol, a styrenated phenol and an activated hindered phenol are compared at the two part level after sunlamp exposure in Figure 6. A styrenated phenol, when used in combination with safflower oil appeared to give the best protection against discoloration after exposure under a sunlamp. These results proved to be misleading, however. The samples, before and after exposure for 6 months indoors in a window subject to the rays of sunlight in Delaware, are shown in Figure 7. It became evident that the methylene-bis(ethyl butyl phenol) offered the best protection against discoloration to natural light, followed closely by the methylene-bis (methyl butyl phenol). The other antioxidants were all about equivalent, and offered less protection.

Other stabilizers.—Many commercially available stabilizers for chlorine-bearing polymers have been evaluated in the past for their effect on the stability

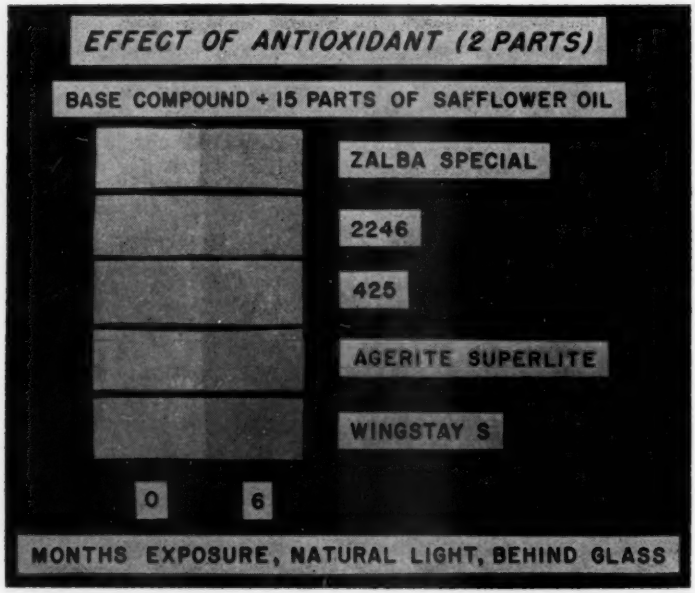

EFFECT OF ANTIOXIDANT (2 PARTS)
BASE COMPOUND + 15 PARTS OF SAFFLOWER OIL
ZALBA SPECIAL
2246
425
AGERITE SUPERLITE
WINGSTAY S
0
6
MONTHS EXPOSURE, NATURAL LIGHT, BEHIND GLASS

Fig. 7.

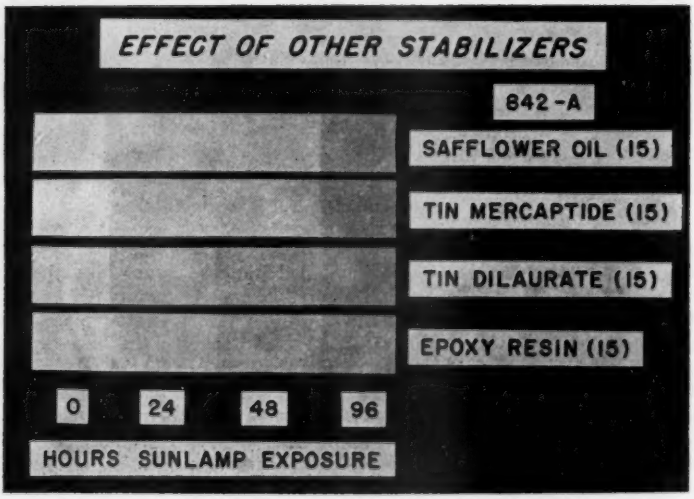

EFFECT OF OTHER STABILIZERS
842-A
SAFFLOWER OIL (15)
TIN MERCAPTIDE (15)
TIN DILAURATE (15)
EPOXY RESIN (15)
0
24
48
96
HOURS SUNLAMP EXPOSURE

Fig. 8.

of neoprene against discoloration during exposure to sunlight. None of the ultraviolet absorber types and few of the organo-metallic compounds tried were of significant value. Ultraviolet absorbers actually increased the rate of discoloration by interfering with the normal bleaching action of sunlight on light-colored neoprene samples. Three stabilizers which did inhibit discoloration were butyl tin dilauryl mercaptide, dibutyl tin dilaurate and liquid epoxy resins. Their effects on an 842A latex compound at the 15 part level compared to 15 parts of safflower oil are shown in Figure 8 after sunlamp exposure for 24, 48 and 96 hours. Although essentially as effective as safflower oil in preventing discoloration, their use in the required amounts generally may be regarded as impractical because they retard the cure of neoprene.

Synergism.—Combinations of stabilizers have been known to exhibit synergism with respect to the stability of light-sensitive materials. Dibutyl

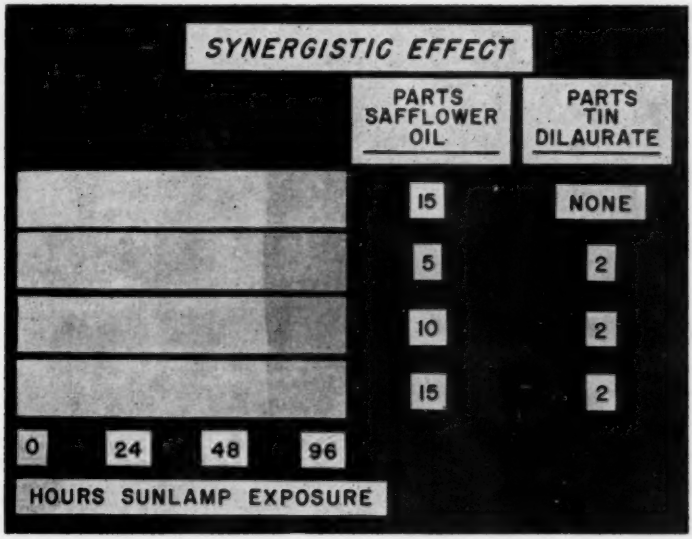


Fig. 9.

tin dilauryl mercaptide, dibutyl tin dilaurate, and a liquid epoxy resin were studied in combinations with safflower oil in neoprene for evidence of a synergism. The effects of 5, 10 and 15 parts of safflower oil in combination with 2 parts of dibutyl tin dilaurate were studied in comparison to those of 15 parts of safflower oil without the dilaurate in a Neoprene Latex 842A compound. Results after exposure for 24, 48 and 96 hours under the sunlamp are shown in Figure 9. Synergism was evident by the fact that 5 parts of safflower oil and 2 parts of dibutyl tin dilaurate were as effective in reducing discoloration as 15 parts of safflower oil.

Accelerators and Curing Conditions.—Many different accelerator combinations, curing times and temperatures are used for neoprene latex products. The following three commonly used accelerator combinations were evaluated

for their effect on the discoloration of a Neoprene Latex 842A compound containing 15 parts of safflower oil:

1. Sodium dibutyldithiocarbamate	1 part
Thiocarbanilide	1 part
2. Sodium dibutyldithiocarbamate	1 part
Tetraethylthiuram disulfide	1 part
3. Zinc dibutyldithiocarbamate	2 parts

The samples and an unaccelerated control were cured for 60 minutes at 120° C and exposed in a Weather-O-Meter (dry) for 24, 48 and 96 hours. Results are shown in Figure 10. Note that the accelerator systems studied did not appreciably affect discoloration.

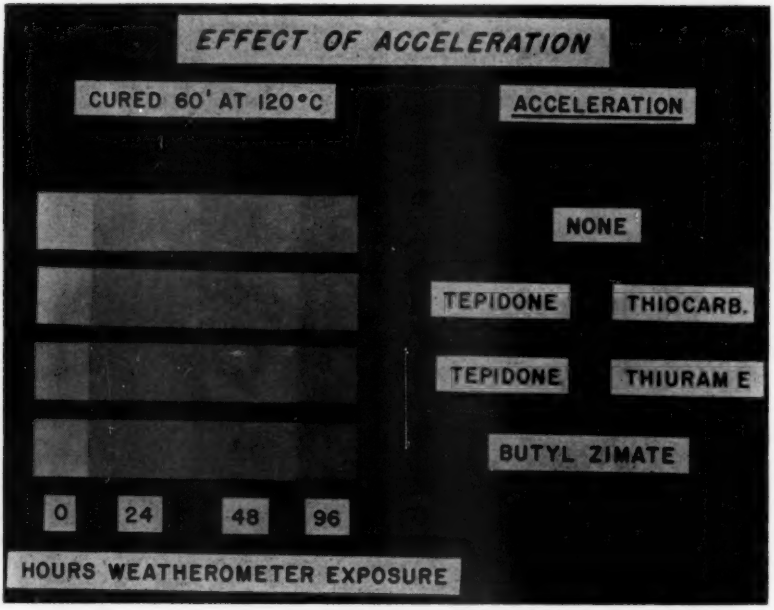


Fig. 10.

The effect of curing temperature was studied next. A Neoprene Latex 842A compound containing safflower oil and accelerated with one part each of sodium dibutyldithiocarbamate and thiocarbanilide was cured at 100° C, 120° C, and 140° C. Results are shown in Figure 11 before and after exposure in a Weather-O-Meter for 24, 48 and 96 hours. Note that up to 120° C, curing temperature did not affect discoloration, but at 140° C some discoloration in light resulted.

Neoprene latex types.—The initial color and tendency to discolor in light is known to vary with the type of neoprene latex used. Neoprene Latex 400 is the most resistant to discoloration of all the types, followed in order by Neo-

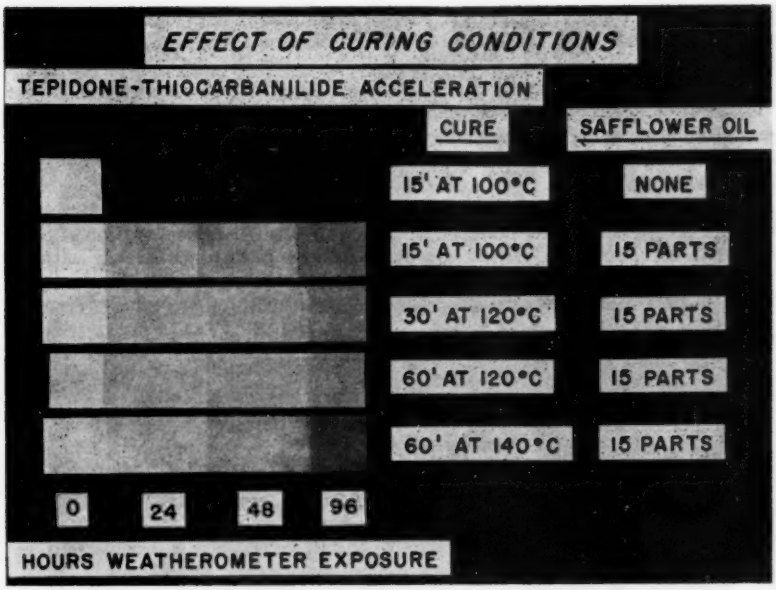

EFFECT OF CURING CONDITIONS
TEPIDONE-THIOCARBANILIDE ACCELERATION
CURE
SAFFLOWER OIL
15' AT 100°C
NONE
15' AT 100°C
15 PARTS
30' AT 120°C
15 PARTS
60' AT 120°C
15 PARTS
60' AT 140°C
15 PARTS
0
24
48
96
HOURS WEATHEROMETER EXPOSURE

Fig. 11.

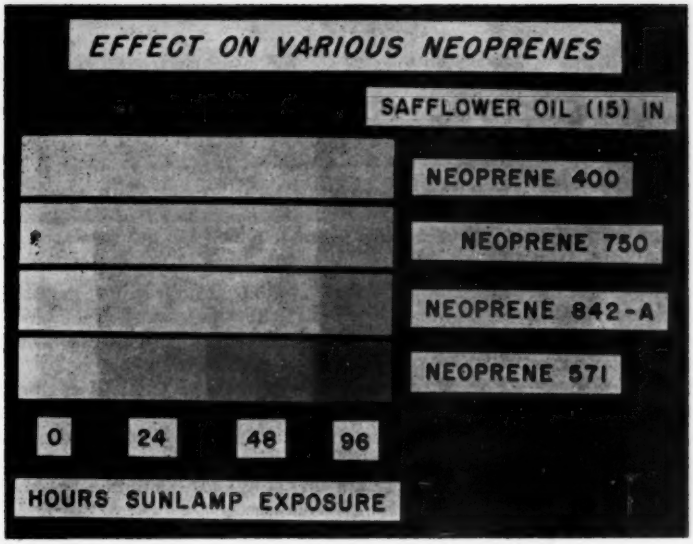

EFFECT ON VARIOUS NEOPRENES
SAFFLOWER OIL (15) IN
NEOPRENE 400
NEOPRENE 750
NEOPRENE 842-A
NEOPRENE 571
0
24
48
96
HOURS SUNLAMP EXPOSURE

Fig. 12.

prene Latexes 750, 842A and 571. When compounded with safflower oil, their relative positions with respect to discoloration remained unchanged as shown in Figure 12.

Natural rubber, SBR and NBR latexes.—The effect of safflower oil on the discoloration of natural rubber, SBR and NBR latex compounds in sunlight was studied next. Products made from these elastomers generally have been considered more resistant to discoloration on exposure to light than products made from neoprene. Specimens before and after six months exposure in sunlight indoors behind glass in Delaware are shown in Figure 13. It will be noted, first, that safflower oil did not appear to affect the discoloration of SBR or NBR compounds. Neither did it affect natural rubber which, with or

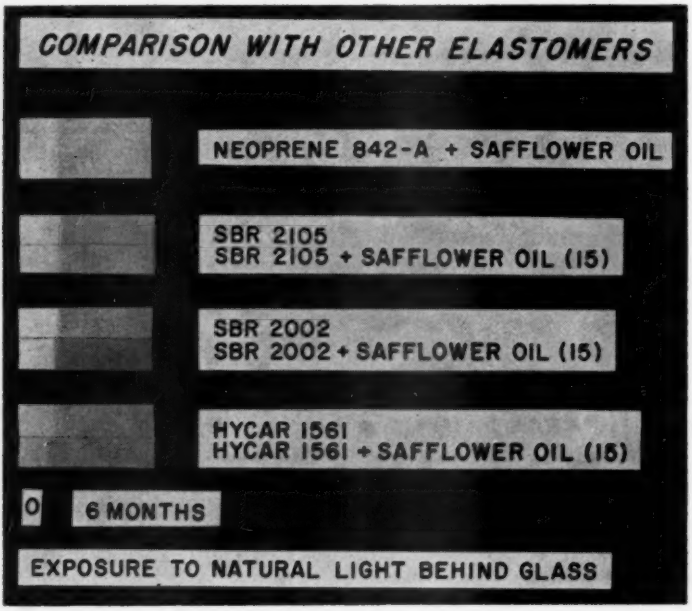


Fig. 13.

without safflower oil, discolored the least. Neither natural rubber specimen is shown—they became very gummy. Of particular note is the fact that the neoprene specimen protected with safflower oil resisted discoloration as well as any of the SBR or NBR specimens.

Effect of safflower oil on physical properties.—Organic fluids, if compatible, generally function as plasticizers for neoprene compounds; reducing modulus, tensile strength and increasing the elongation at break. Safflower oil reduced modulus and tensile strength as expected but did not affect the elongation at break as shown by the stress-strain data in Table I for Neoprene Latex 842A films containing 0, 5, 10 and 15 parts of safflower oil.

Safflower oil markedly enhanced the resistance of neoprene to heat aging as shown by the stress-strain data in Table I after aging specimens in an air

TABLE I

STRESS-STRAIN PROPERTIES OF NEOPRENE LATEX 842A FILMS

Neoprene 842A (solids basis)	100	100	100	100
Aquarex SMO	3	3	3	3
Antioxidant	2	2	2	2
Zinc oxide	10	10	10	10
Titanium dioxide	20	20	20	20
Tepidone	1	1	1	1
Thiocarbanilide	1	1	1	1
Safflower Oil	None	5	10	15
Coagulant dipped films, leached in water 2 hours at 40° C, dried 4 hours at 70° C, and cured 60 minutes at 120° C.				
Stress at 300% elongation, psi				
Original	375	350	300	275
Aged 7 days at 100° C	575	525	500	475
Aged 14 days at 100° C	650	600	575	550
Tensile strength, psi				
Original	2600	2500	2200	1900
Aged 7 days at 100° C	1800	1600	1500	1400
Aged 14 days at 100° C	1300	1200	1175	1100
Ultimate elongation, %				
Original	880	880	890	880
Aged 7 days at 100° C	525	575	600	650
Aged 14 days at 100° C	375	400	450	500

oven for 7 and 14 days at 100° C. This phenomenon will be the subject of a subsequent paper[3]. Other effects of safflower oil shown in Table II are increased resistance to ozone attack and reduced brittleness temperature.

Fungus attack.—Vegetable oils are known to be nutrients for fungi. It is not surprising, therefore, that neoprene vulcanizates containing them develop a fungus growth on outdoor exposure, although none has been observed indoors. Neoprene compounds containing vegetable oils are not suggested for use where exposure conditions are conducive to fungus growth. A search for an effective fungicide as well as other effective stabilizers against discoloration in light that are non-nutrients is in progress.

ABSTRACT

The tendency for light-colored neoprene vulcanizates made from latex to discolor when exposed to light was inhibited markedly by compounding with triglycerides of long chain fatty acids in combination with non-discoloring

TABLE II

OZONE RESISTANCE AND BRITTLENESS TEMPERATURE
NEOPRENE LATEX 842A FILMS

Base Compound + Tepidone (1) and thiocarbanilide (1)
Cured 60 minutes at 120° C

Parts of safflower oil	None	5	10	15
3 ppm. ozone, 40% strain Hours to 1st crack	45	180	300+	300+
Brittleness Temperature, ° C	−40	−45	−49	−53

antioxidants. Effectiveness increased with the degree of unsaturation of the fatty acid up to two double bonds (safflower oil). Resistance to discolorations increased with increasing amounts of oil up to 15 parts. Both the ester linkage and the degree of unsaturation in vegetable oil appeared to influence stability in light. Organo tin compounds were found which functioned synergistically with safflower oil. Discoloration of safflower oil stabilized neoprene latex compounds was not affected appreciably by commonly used acceleration systems, nor by varying the curing conditions up to 120° C. Safflower oil reduced discoloration in all neoprene latex types. Neoprene latex compounds containing safflower oil discolored in sunlight no more than those of SBR or NBR latex. Safflower oil did not affect the discoloration of natural rubber, SBR or NBR latex compounds in sunlight.

Other effects of safflower oil on the cured properties of neoprene latex films were reduced modulus and tensile strength but without change in elongation, enhanced heat and ozone resistance and lower brittle temperature.

REFERENCES

[1] Forman, D. B. and Torrence, M. F., Report 49-1, Rubber Chemicals Div., E. I. du Pont de Nemours & Co.
[2] Murray, R. M., Rubber Chem. & Technol. **32**, No. 4 (1959).
[3] Seligman, K. L. and Roussel, P. A., Paper presented before the Division of Rubber Chemistry of the American Chemical Society, April 19–21, 1961 at Louisville, Kentucky; following paper, this issue.
[4] Thompson, D. C., Baker, R. H. and Brownlow, R. H., *Ind. Eng. Chem.* **44**, 850 (1952).
[5] U. S. Patent No. 1,908,719 (expired April 2, 1952).
[6] U. S. Patent No. 2,692,250.
[7] Walter, H. C., Mantell, J. and Gladding, E. K., Paper presented at the Gordon Research Conference, 1952

STABILIZATION OF NEOPRENE. II. PROTECTION OF NEOPRENE VULCANIZATES AGAINST HEAT AGING *

K. L. Seligman and P. A. Roussel

E. I. du Pont de Nemours & Company, Inc., Elastomer Chemicals Department, Wilmington, Delaware

INTRODUCTION

Neoprene, a high molecular weight elastomeric polymer of 2-chlorobutadiene-1,3 (chloroprene) has been used for many years in applications where a high degree of heat resistance was required in combination with oil and ozone resistance, as well as a high level of elastomeric properties. Research efforts have been directed to improve the heat resistance of neoprene and have provided two stabilizing systems of general applicability. The first of these resulted from the discovery[1] that high molecular weight aliphatic esters, particularly fatty acid glycerides, greatly improve the resistance of neoprene toward sunlight discoloration. Esters used to improve the heat resistance of neoprene must be inert when exposed to elevated temperatures. From results to be cited it appears that physical or chemical behavior which reduces the effectiveness of the ester as a plasticizer also reduces the effectiveness as a stabilizer. In order to be useful, these esters should have: (1) a low degree of volatility and (2) little tendency to air-oxidize and crosslink. Certain readily available, naturally occurring fatty acid glycerides such as safflower and rape seed oil are particularly attractive.

The second stabilizing system is based upon the hypothesis that oxidative degradation during the heat aging of neoprene is connected with labile chlorine sites formed by the 1,2-polymerization of chloroprene[3]. The bis-alkylation theory of neoprene vulcanization[2, 4] stipulates that these sites are also involved in the cure. Incomplete removal of these labile chlorines during cure leaves residual moieties prone to undergo several different kinds of oxidative attack. Exhaustive removal of the labile chlorines with either a high curative level or an auxiliary reagent capable of reacting with residual labile chlorines brings about an improvement in the heat resistance of neoprene. Dodecyl mercaptan has been found to be of value as such an auxiliary reagent.

EXPERIMENTAL

Materials.—All chemicals and compounding ingredients used were of commercial quality. The trivial and trade names, chemical equivalent, and source of supply for these are:

Neoprene Type W, E. I. du Pont de Nemours & Co.
NA-22, ethylene thiourea, E. I. du Pont de Nemours & Co.

* Paper presented before the Division of Rubber Chemistry, American Chemical Society, April 19–21, 1961, Louisville, Ky. Contribution No. 109. The address of the senior author is now the Beaumont Works of the E. I. du Pont de Nemours and Co., P. O. Box 3269, Beaumont, Texas.

Neozone A, N-phenyl-1-naphthylamine, E. I. du Pont de Nemours & Co.

Safflower oil, glyceride with 76% linoleic acid, 14% oleic acid, 4% stearic acid and 6% palmitic acid. Supplied E. F. Drew & Co., New York, N. Y.

Rape seed oil, glyceride with 51% erucic acid, 8% linolenic acid, 14% linoleic acid, 17% oleic acid, 2% saturated acid. Supplied by E. F. Drew & Co., New York, N. Y.

Aranox, *p*-(*p*-tolylsulphonylamido)diphenylamine, Naugatuck Chemical, Div. of U.S. Rubber Co., Naugatuck, Conn.

Octamine, condensation product of diphenylamine and di-isobutylene, Naugatuck Chemical, Div. of U. S. Rubber Co., Naugatuck, Conn.

Naphthenic petroleum oil, Circo Oil, Sun Oil Co., Philadelphia, Pa.

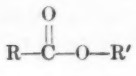
Aromatic petroleum oil, Sundex 85, Sun Oil Co., Philadelphia, Pa.

Test methods.—All tests were carried out by standard ASTM procedures. All aging evaluations were carried out according to the "Method of Heat Aging of Vulcanized Natural or Synthetic Rubber by Test Tube Method", ASTM D865-57.

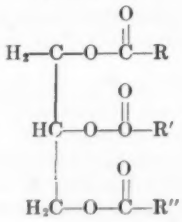
Compound formulations.—Four compounding formulations were employed with this work. They are given in Table I. The stocks were cured for either 30 or 40 minutes at 153° C.

Stabilizing effect of esters.—The resistance of neoprene toward heat aging can be markedly improved by incorporation of esters into the compound. Concentrations of the order of 15 phr have been employed. Three types of high molecular weight esters have been evaluated. They are: (1) the monoesters, shown as compound A, of which methyl oleate and methyl stearate are representative, (2) the triesters, Compound B, represented by the glycerides and (3) the tetraesters, Compound C, i.e., pentaerythrityl tetrastearate.

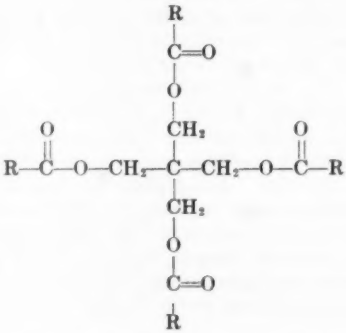
Compound A



Compound B



Compound C



The change of the two important properties affected by the heat aging process, i.e., modulus and elongation at break, were determined periodically by obtaining stress-strain data on vulcanized stocks aged at 121° C. For brevity, only the relative elongation at break will be discussed; none of the conclusions would be altered by considering the rate of change in the modulus. Changes in the values of these and other stress-strain properties for selected compounds are shown in Table III.

Figure 1 presents data on the aging of 121° C of clay filled stocks containing a number of esters. The relative elongation at break is plotted vs. days at

TABLE I

COMPOUNDING FORMULATIONS

	Gum stock Compound A	Clay stock Compound B	Black stocks Compound C	Black stocks Compound D
Neoprene Type W	100	100	100	100
Neozone A	2	2	As shown	—
Aranox	—	—	As shown	1
Octamine	—	—	As shown	4
Stearic acid	—	0.25–0.5	—	0.5
Paraffin wax	—	1	—	—
Petrolatum	—	1	—	—
Suprex Clay	—	90	—	—
MT carbon black	—	—	50	50
Atomite whiting	—	—	—	50
MgO	4	4	4	4
ZnO	5	5	10	10
Circo Oil	—	12	—	—
Sundex 85	—	—	10	As shown
NA-22	As shown	As shown	As shown	1

121° C. When plotting aging data of neoprene in this manner, it is usually observed that the elongation at break does not change quickly during the early stages of the aging process. After this "induction" period a much more rapid change in the elongation at break occurs followed by a decrease in the rate with prolonged aging. This behavior is well illustrated by the control stock in Figure 1 which contains 12 phr of process oil.

It has usually been observed that materials which are effective in improving the heat resistance of neoprene do so by prolonging the initial induction period; they have little effect on the rate of change of the elongation at break once the

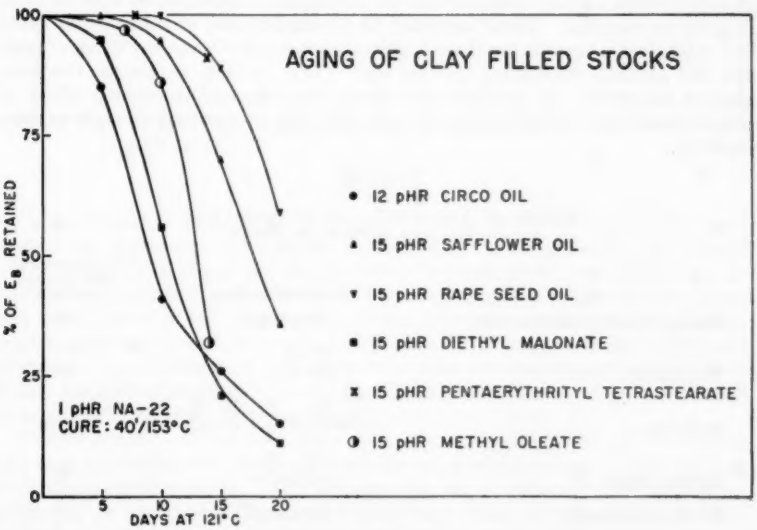


FIG. 1.

induction period is terminated. These considerations are of practical importance, since the initial period during which little change occurs in the properties of the finished neoprene article can be extended considerably by the use of stabilizers.

It can be seen from Figure 1 that the relatively low molecular weight esters, methyl oleate and diethyl malonate, enhance the heat resistance during the early stages of aging, but offer little improvement with prolonged aging. It is believed that these esters are volatilized on prolonged heat aging whereby the vulcanizate loses its stabilizer as well as its plasticizer. The esters having a lower degree of volatility, such as safflower oil, rape seed oil and pentaerythrityl tetrastearate, do improve the heat resistance of neoprene. They are particularly effective in prolonging the initial time interval during which the elongation at break changes relatively little.

A hypothesis for the difference in the behavior of these high molecular weight esters is based upon the degree of unsaturation of these esters and their tendency to air oxidize and crosslink. Air-oxidation and crosslinking are typical of the unsaturated fatty acid glycerides and it is this property which makes them highly valuable as drying oils. Support for this hypothesis is shown in Table II. Pentaerythrityl tetrastearate and rape seed oil show the least change in the elongation at break after 14 days at 121° C. This superiority over safflower oil can be rationalized on the basis of their lower degree of unsaturation. Pentaerythrityl tetrastearate does not contain any unsaturation and can be expected to impart excellent heat stability to neoprene. Rape seed oil, which predominantly is an ester of erucic acid, contains only a single double bond and is essentially equivalent to the tetrastearate in improving the heat resistance of neoprene. Safflower oil, which contains two nonconjugated double bonds (linoleic acid ester), does have a beneficial effect on the heat resistance but is not as effective as the less unsaturated glycerides. Use of some glycerides having multiple and/or conjugated unsaturation such as tung oil must be avoided. Their tendency to air-oxidize and crosslink is so great that vulcanizates containing these highly unsaturated oils appear to age faster than the controls containing process oil. They, in fact, accelerate the heat aging of neoprene. As pointed out above, the lessened stabilizing effect of methyl oleate and diethyl malonate probably can be ascribed to their greater volatility.

TABLE II

EFFECT OF VOLATILITY AND UNSATURATION ON STABILIZING ACTION OF ESTERS

Oil	Structural features	% E_B retained after 14 days at 121° C
Pentaerythrityl tetrastearate	Saturated	90
Rape seed	$-\overset{H}{C}=\overset{H}{C}-$	90
Safflower	$-\overset{H}{C}=\overset{H}{C}-CH_2-\overset{H}{C}=\overset{H}{C}-$	65–70
Methyl oleate	$-\overset{H}{C}=\overset{H}{C}-$	42
Diethyl malonate	Saturated	25
Process oil	Naphthenic	28

Table II also shows that neoprene vulcanizates containing 15 phr of rape seed oil apparently are better by a factor of three after 14 days at 121° C than vulcanizates containing 12 phr of a hydrocarbon process oil.

In Figure 2 is compared the aging at 121° C of a high quality neoprene black stock with no oil which contains the Aranox-Octamine antioxidant system, with the same stock containing 15 phr of rape seed oil It is apparent that the vulcanizate containing rape seed oil ages considerably better than the one without any oil. During the initial aging period the elongation at break of the stock containing the rape seed oil increases somewhat but after 21 days at 121° C the rape seed oil vulcanizate has retained 87% of its elongation while the one without oil has retained only 46%.

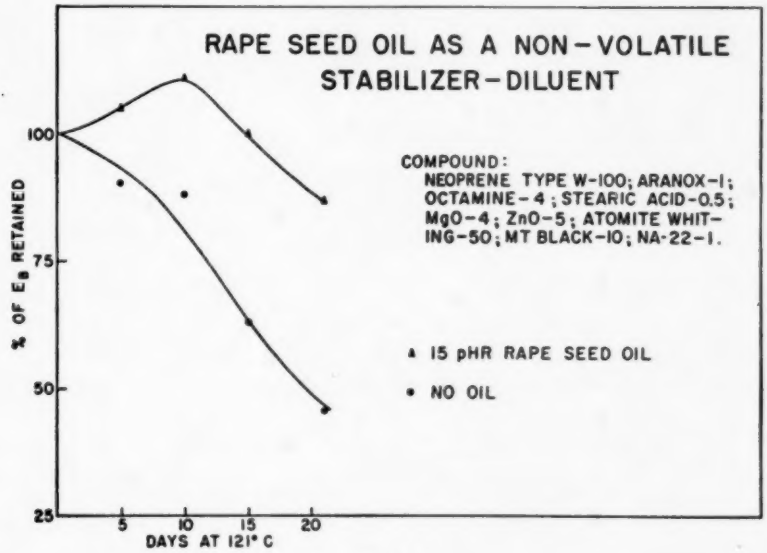


Fig. 2.

Concentration of ester required.—The optimum concentration of the ester required for maximum stabilization as determined with safflower oil is about 15 phr, as shown in Figure 3. As 15 parts of process oil in a clay filled vulcanizate are replaced with safflower oil in 5 part increments, improvement occurs until the 15 parts of the process oil are completely replaced with safflower oil. Further addition of safflower oil provides only minor improvement in the heat resistance. A combination of 5 parts of process oil and 10 parts of safflower oil also appears attractive. The stress-strain properties of these compounds are not greatly affected by these changes.

Fungus growth.—It has been observed that neoprene vulcanizates containing fatty acid glycerides are prone to attack by fungi when exposed outdoors or in warm moist environments. At this time the use of fatty acid glycerides for improving the resistance of neoprene toward heat aging cannot be recommended for those applications where prolonged exposure to the above environmental

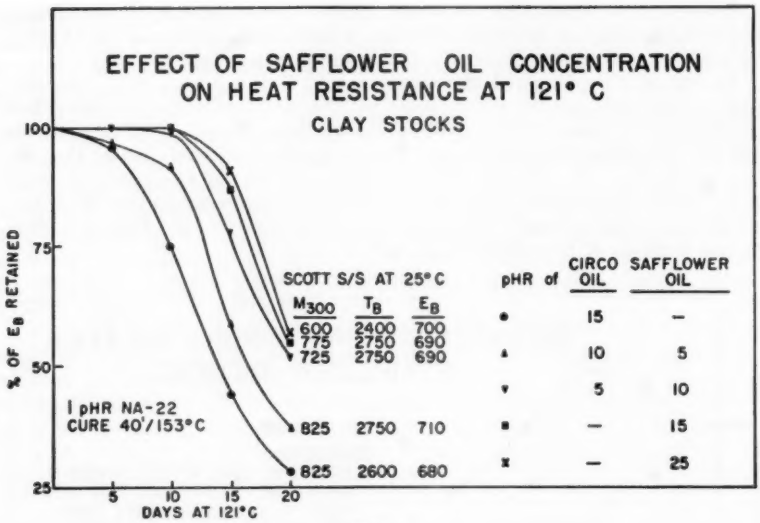


FIG. 3.

conditions is expected. Efforts are continuing to find means to eliminate this problem.

Exhaustive removal of allylic chlorine.—The majority of commercially available neoprenes possess about 0.66–0.70% of "labile chlorine" (0.0186–0.0197 atom of chlorine/100 g of polymer), attributed to an allylic chloride structure[3].

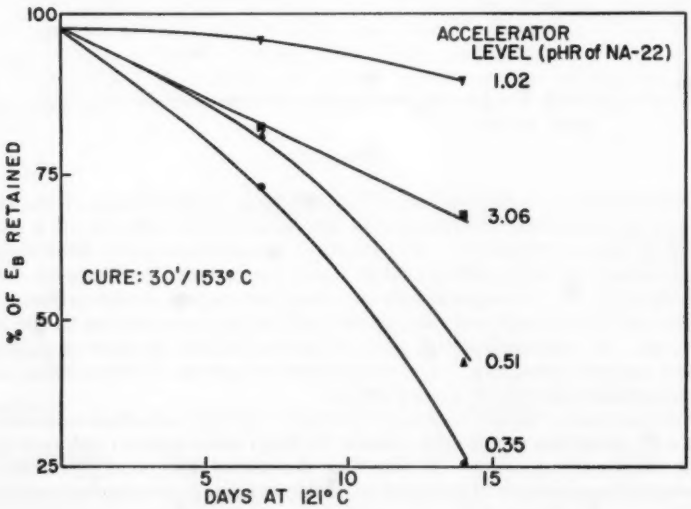


FIG. 4.

This allylic chloride structure is the result of the 1,2-polymerization of chloroprene and occurs to an extent of about 1.5% in these polymers.

The bis-alkylation theory of neoprene curing[2] postulates that these allylic chlorine sites are also the reactive sites for crosslinking with reagents[4] such as ethylenethiourea (NA-22). These allylic chlorines can therefore be essentially completely removed with a sufficiently high level of curing agent. It was expected that a comparison of the best aging response of conventionally and exhaustively cured neoprene would reveal at least qualitatively the contribution made to aging stability by residual labile chlorine. The results obtained on a gum stock are shown in Figure 4.

It is clear that exhaustive curing of neoprene improves profoundly the neoprene's stability to heat aging at 121° C. The exhaustively cured neoprenes are "over-cured" by conventional standards, but the relative change in the

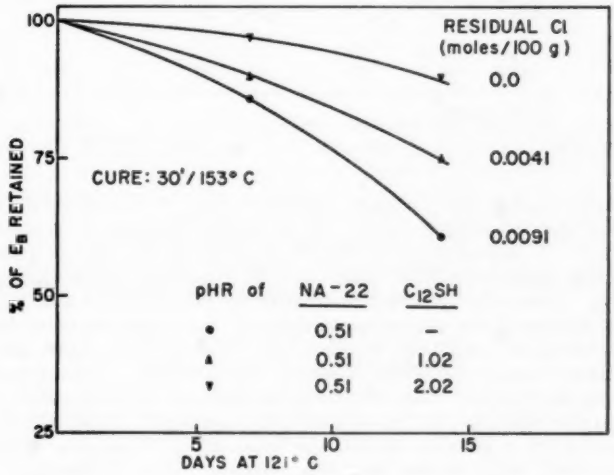


FIG. 5.

elongation at break provides a convenient means for evaluating heat resistance. The heat stability of the vulcanizate is at a maximum at the concentration of NA-22 (1.02 phr) which is stoichiometrically equivalent to the concentration of allylic chlorine. It appears that an increase or decrease from that level impairs stability.

Auxiliary reagents: Dodecyl mercaptan.—The maximum stability of neoprene at 121° C occurred at the stoichiometric level of NA-22, a curative level which may provide an impractically high state of cure. Auxiliary reagents which would consume residual allylic chlorine but which would not overcure neoprene were therefore sought. Of necessity these reagents had to be monofunctional in respect to attack on the allylic chlorine, and their rate of reaction with allylic chlorine had to be considerably slower than that of the curing agent. Otherwise, a decline in both the state and rate of cure could be expected.

Of those reagents investigated dodecyl mercaptan was found to meet these requirements best. The data in Figure 5 show that this mercaptan used with

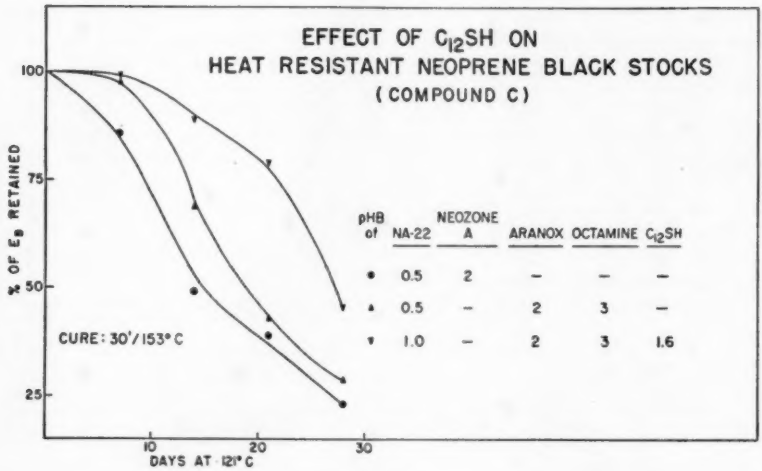


FIG. 6.

NA-22 as the curing agent, imparts the same order of heat aging stability to neoprene as does exhaustive curing with NA-22 but without an increase in the state of cure. It is seen that the heat resistance of these neoprene gum stocks at a constant accelerator level improves with increasing concentration of the mercaptan. It may be significant that, as in the exhaustively cured neoprenes previously discussed, the maximum resistance to heat aging occurred when the total equivalents of NA-22 and the mercaptan were at least equivalent to the molar concentration of the labile chlorine in the polymer. Under these conditions it can be expected that essentially no residual allylic chlorine remains in the polymer and that heat resistance will be greatest. Dodecyl mercaptan also improves by a sizeable margin the resistance of Neoprene Type W to accelerated heat aging in clay and black stocks. Figure 6 presents data on black stocks containing the Aranox-Octamine antioxidant system. Addition of 1.6 parts dodecyl mercaptan to the two-component antioxidant provides a sizeable improvement in heat resistance. The accelerator level in the stocks containing the dodecyl mercaptan has to be increased in order to overcome its slight retardation of the cure rate.

Theoretical considerations.—The function of the mercaptan in the RSH/NA-22 curing system which improves the stability of neoprene at elevated temperature has not been proved. However, the mercaptans which are effective with NA-22 are known in model systems[5] to react readily with the kind of "labile" chlorines believed to be the cure sites in neoprene. It seems reasonable, therefore, that the protection afforded by the RSH/NA-22 curing system is related to the reaction of the RSH compounds with some of neoprene's labile chlorine.

Additive effect of dodecyl mercaptan-rape seed oil.—The stabilizing effects of the two systems under discussion for increasing the heat resistance of Neoprene Type W are additive as shown in Figure 7. The various materials were evaluated in a black stock, Compound D, containing the Aranox-Octamine

TABLE III

CHANGE IN STRESS-STRAIN PROPERTIES WITH AGING OF STOCKS CONTAINING RSH AND RAPE SEED OIL (COMPOUND D)

Stabilizers					
$C_{12}H_{25}SH$		—	—	1.5	1.5
$(C_8)_2S$		—	—	2.0	2.0
Rape seed oil		—	15	—	15
Aromatic petroleum oil		15	—	15	—
Cure: 40′/153°					
After tube aging at 121° C for					
0 Days	M_{300} (psi)	750	875	550	625
	T_B (psi)	1400	1475	1450	1475
	E_B (%)	510	420	660	520
10 Days	M_{300} (psi)	1000	875	775	650
	T_B (psi)	1200	1200	1150	1200
	E_B (%)	410	410	600	600
21 Days	M_{300} (psi)	—	—	—	950
	T_B (psi)	1375	1075	1100	1000
	E_B (%)	190	250	280	380

antioxidant system. In this particular instance the addition of dodecyl mercaptan and dioctyl sulfide to the basic recipe containing the aromatic petroleum oil provided an improvement over the short aging period. (Dioctyl sulfide at times has been found to augment the stabilizing action of dodecyl mercaptan.) This improvement was considerably smaller than the substitution of the 15 parts of the aromatic petroleum oil with 15 parts of rape seed oil. The combination, however, of dodecyl mercaptan-dioctyl sulfide-rape seed oil has outstanding resistance to accelerated heat aging at 121° C. This com-

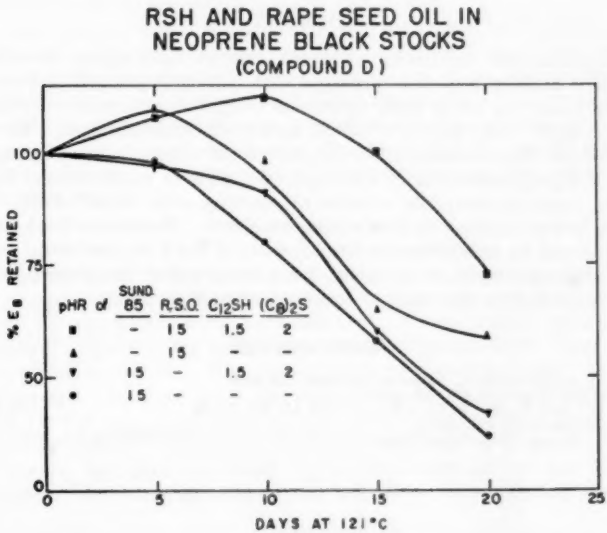


FIG. 7.

pound after aging for 15 days at 121° C has suffered essentially no change in its elongation at break. After 21 days it has approximately twice the elongation compared to the control compound not containing these stabilizers.

Again it is observed that the elongation at break of the vulcanizates containing the rape seed oil increases slightly during the early aging period. This, however, has a negligible effect on the other properties. The actual changes in stress-strain properties of these vulcanizates are shown in Table III. The tensile strength of the stabilized vulcanizates after 21 days has changed more than that of the control stock but not to an extent which can be considered serious. After 10 days at 121° C the tensile strength of all stocks has decreased approximately the same amount. The lower state of cure of the dodecyl mercaptan containing stocks is evident by their lower moduli. Rape seed oil alleviates this retardation of the cure rate to a minor degree as indicated by the original elongations at break. The stocks containing rape seed oil suffered essentially no change in modulus after aging for 10 days at 121° C although the elongation at break of the vulcanizates containing both stabilizing systems increased by about 15%.

CONCLUSION

Fatty acid glycerides, in particular rape seed oil, improve the resistance of Neoprene Type W against accelerated heat aging. Dodecyl mercaptan added in small quantities to gum, clay and black filled neoprene stocks also exerts a considerable stabilizing effect. Either method can be used for applications where an enhancement in the heat resistance of neoprene is desirable. Vegetable oils should not be employed in applications where potential fungus growth is a problem. The two stabilizing systems in combination are attractive when the maximum heat resistance is required.

SUMMARY

Two systems for stabilizing neoprene against heat aging have been investigated. Both systems are employed with conventional antioxidants. One method is based on using high molecular weight esters, particularly certain readily available fatty acid glycerides, as the stabilizer-diluent. The second method is based on the removal during cure of the allylic chlorine formed as the result of 1,2-polymerization of chloroprene. This is accomplished by introduction of auxiliary reagents capable of reacting with those allylic chlorines which are not consumed by the curing reaction. Maximum heat resistance can be obtained by simultaneous employment of the two methods. Improvements of the order of 1½ to 2½ times the normal useful life of neoprene goods might be expected on the basis of these experimental results.

REFERENCES

[1] Becker, R. O. and Seligman, K. L., preceding paper, this issue.
[2] Kovacic, P., *Ind. Eng. Chem.* 47, 1090 (1955).
[3] Maynard, J. T. and Mochel, W. E., *J. Polymer Sci.* 13, 251 (1951).
[4] Pariser, R., *Kunstoffe* 50, 623 (1960).
[5] Reid, E. E., "Organic Chemistry of Bivalent Sulfur", Vol. I, Chemical Publishing Co., New York, N. Y., 1958.

INFLUENCE OF VULCANIZATION ON ADHESION TO NON-VULCANIZING POLYMERS *

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According to contemporary ideas[1–3] the mechanisms of adhesion and covulcanization of rubbers have much in common. The phenomenon of covulcanization, like that of adhesion of polymers, includes the diffusion of macromolecules and of segments of them, which is particularly intensive in the initial period of vulcanization, when the crosslinks have not yet formed. The difference between covulcanization and adhesion lies solely in the fact that the process of interpenetration of the molecular chains in the former case is sooner or later broken off by the vulcanization process being superimposed upon it, securing the macromolecules or portions of them by strong chemical bonds. This leads to the formation of an adhesion joint considerably superior in strength to a joint in which the molecules diffusing through are attached only by weak intermolecular bonds.

It is important to ascertain what is the influence of the vulcanization of elastomers upon their adhesion to polymers not capable of forming chemical bonds with them. This case is of immense practical importance, since unvulcanized rubbers are very often used in combination with vegetable and synthetic fibers which are not capable of vulcanizing.

As adhesives we selected elastomers of varying molecular structure, polarity and degree of molecular mobility: butadiene-acrylonitrile rubber (SKN-26), butadiene-styrene rubber (SKS-30A), butadiene-styrene oil-extended rubber (SKS-30ARM-15) and butyl rubber. Using these rubbers we prepared stocks both containing and not containing vulcanizing groups (in the latter case the components of the vulcanizing groups were replaced by an equal quantity of inert filler—whiting). The amount of vulcanizing group was set at the optimum for each rubber.

The substrates used were films containing no plasticizers—cellophane (cellulose hydrate) and Perfol' PK-4 (polycaprolactam).

The adhesive was applied to the substrate by coating on a calender at the optimum conditions for each elastomer[4]. The specimens produced in this way were plied up and subjected to vulcanization. Vulcanization was carried out in a Berstorff apparatus for continuous vulcanization at 143° C and a specific pressure $\approx$ 0.85 kg/sq cm. The time of cure was varied between 0 and 88 min.

In Figures 1 and 2 we show the dependence of the specific adhesion (determined by the ply separation) of the elastomeric coatings to the abovementioned substrates. As may be seen, independently of the type of adhesive and substrate, the time for which the joint is kept at the temperature of vulcanization very strongly affects the adhesion. Nevertheless even if the

* Translated by R. J. Moseley from *Doklady Akad. Nauk SSSR* **135**, 133–6 (1960); RAPRA translation 871.

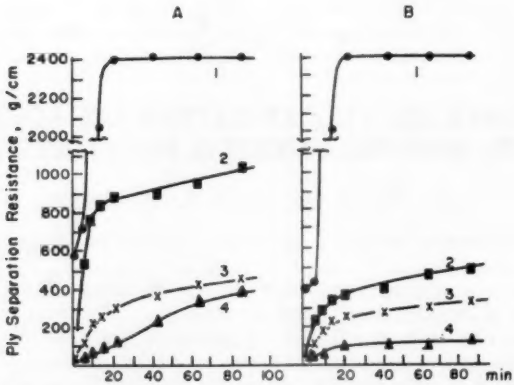

FIG. 1.—Influence of time of thermal treatment upon the adhesion of coatings not containing vulcanizing groups to (a) PK-4 polyamide film, (b) cellophane. *1*—Butyl rubber; *2*—butadiene-styrene oil-extended rubber SKS-30ARM-15; *3*—butadiene-styrene rubber SKS-30A; *4*—butadiene-acrylonitrile rubber SKN-26.

adhesion of coatings not containing vulcanizing groups increases continuously (but with varying rate) as the time of thermal treatment increases, the adhesion of coatings which do contain vulcanization groups passes through a maximum.

The continuous increase in the adhesion value in the former case may be governed by the interdiffusion of molecules or their elements in the boundary layer. In the latter case the enhancement of adhesion in non-protracted thermal treatment of a joint is explained evidently by the same cause as in the former case. In this stage, as a result of the presence of an induction period of vulcanization, the processes of structurization apparently either do not yet take place or proceed to a very small extent.

The sharp alteration in the shape of the curve in vulcanization beyond 12 to 15 min is caused probably by two factors. One of these factors is the sharp reduction in the rate of diffusion as a result of the structurization of the adhesive. Nevertheless even complete cessation of diffusion might only mean that starting at a certain instant the adhesion would stop rising, in spite of the

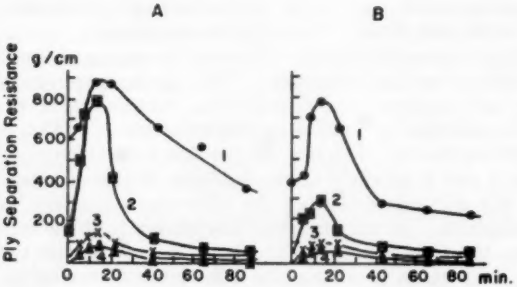

FIG. 2.—Influence of vulcanization upon adhesion of a vulcanized rubber coating to (a) PK-4 polyamide film, (b) cellophane. *1*—Butyl rubber; *2*—butadiene-styrene oil-extended rubber SKS-30ARM-15; *3*—butadiene-styrene rubber SKS-30A; *4*—butadiene-acrylonitrile rubber SKN-26.

increasing time of thermal treatment. One factor controlling the lowering of the adhesion might be the occurrence in the zone of contact of supplementary stresses as a result of the shrinking of the rubber coating, caused by the structurization of the elastomer. These stresses definitely will reduce the force which it is necessary to apply to destroy the adhesion joint.

The data obtained allow us to draw a further series of conclusions relative to the influence of the molecular structure of the elastomers under investigation upon the adhesion.

It is known that butyl rubber is a substantially nonpolar elastomer with linear structure, whose molecular weight is very low in comparison with the molecular weights of other elastomers (the weight average molecular weight of the butyl rubber in our case was 32,000). The low molecular weight of this polymer is responsible for the presence in it of a considerable number of macromolecule ends which, as is known[5], are most active in the processes of diffusion. All this also gives butyl rubber maximum adhesion to both substrates.

The presence of awkward pendant phenyl groups and high molecular weight are responsible for the considerably lower adhesion of butadiene-styrene elastomers. It is very interesting to compare the adhesion of the butadiene-styrene elastomers SKS-30A and SKS-30ARM-15. The latter differs from the ordinary low-temperature butadiene-styrene rubber SKS-30A only in the amount of softener added to the copolymer in the production process. Taking into account that the copolymers under investigation have the same chemical nature, it must be assumed that the higher adhesion of the oil-extended elastomer is governed by the greater mobility of its chain segments.

Finally, minimum adhesion is in all cases found with the most polar adhesive, the butadiene-nitrile copolymer. This circumstance may likewise be explained from the viewpoint of the diffusion theory of adhesion by the low lability of the molecular chains and by the presence of pendant nitrile groups. In this case the processes of diffusion indubitably proceed at a much lower rate, which is shown by a lack of a sharp increase in adhesion in the initial stage of interaction of the polymers. In addition to this the value of the specific adhesion in the latter case may to a significant extent be governed by the intermolecular interaction of the polymers in the contact zone.

It is an essential point that the curves characterizing the alteration in the adhesion value as a function of the time of thermal treatment of the various joints are arranged in the same sequence in Figure 1 and in Figure 2. This means that the peculiarities in the vulcanization of the rubber cannot cover up the influence of the nature of the adhesive upon the adhesion. When we consider the influence of the nature of the substrate upon the adhesion our attention is attracted first of all by the fact that nonpolar rubber exhibits high adhesion to polar substrates. This fact may be explained by the local dissolving of the hydrocarbon chains of the adhesive in the substrate consisting of polar groups and quite large portions of nonpolar hydrocarbon chains[6].

Comparison of adhesion to cellulose and Capron shows that the value is always higher in the case of Capron. In all probability, this is brought about by the exceptional stiffness of the molecular chains of cellulose[7] and the very high density of their packing, owing to the presence of hydrogen bonds between the hydroxyl groups[8]. In addition, in contrast with Capron, cellulose always exists only in a glassy state[7, 9]. Such structure and the physical state of cellulose create extremely unfavorable conditions for the diffusion of elements of molecules of the adhesive.

Thus, the vulcanization of the rubber coating is responsible for the phenomenon of a maximum of adhesion which corresponds to the optimum degree of vulcanization (judged by adhesion). The presence of an optimum of vulcanization (judged by bond strength) was verified by the present authors for rubber-fabric materials on a base of cellulose, Capron and glass fiber. And in these cases also we observed an analogous character of alteration of adhesion as a function of the degree of vulcanization of the rubber. The influence of "mechanical adhesion", while not altering the character of the dependence, leads only to higher values of the total bond strength of the adhesive to fabric in comparison with the corresponding values of the specific adhesion to films.

The presence of an optimum of vulcanization judged by bond strength in rubber-fabric articles and materials may be made use of in production techniques. At the present time vulcanization of such articles is carried out under conditions corresponding to the optimum judged by the physical properties of the rubber. Nevertheless the optimum degree of vulcanization judged by bond strength sets in considerably earlier, and the bond strength under

TABLE 1

INFLUENCE OF DEGREE OF VULCANIZATION UPON RUBBER TO FABRIC BOND STRENGTH

Designation of rubber	Type of carcass fabric	Optimum time of cure in min		Stripping resistance in g/cm after vulcanization	
		for the rubber	for adhesion	35 min	15 min
SKS-30A	Perkal'		15	900	1500
	Capron art. 1520	35	15	350	1050
	T_1 glass fabric		15	600	1350
SKN-26	Perkal'		15	1150	2000
	Capron art. 1520	35–40	15	200	700
	T_1 glass fabric		15	400	1200
Butyl rubber	Perkal'		15	2600	3900
	Capron art. 1520	40	15	2000	3600
	T_1 glass fabric		15	2700	4000

optimum conditions of vulcanization as judged by the properties of the rubber is much lower than its value at the degree of vulcanization corresponding to the adhesion optimum. In Table 1 we give the corresponding values of bond strength of vulcanized rubbers to fabrics of various chemical natures. The bond strength values are given in Table 1, both for vulcanization corresponding to the optimum judged by the properties of the vulcanized rubbers (35 to 40 min at 143°) and for vulcanization under conditions corresponding to the bond strength optimum (15 min at 143°). According to the data in Table 1, reducing the time of cure from 35 to 15 min leads to an increase in the bond strength from 1.8 to 3 fold.

Reducing the degree of vulcanization of these layers (in comparison with the degree of vulcanization of the main body of the rubber) may be achieved without altering the curing conditions now accepted for a given article, by corresponding reduction in the content of vulcanization group in the surface layer of rubber. In addition to the increase in the rubber-fabric bond strength in articles the measure indicated makes it possible to reduce the cost of articles

on account of the reduction in the amount of the expensive ingredients of the vulcanizing group.

REFERENCES

[1] Voyutskiĭ, S. S. and Shtarkh, B. V., *Kolloid Zhur.* **16**, 3–9 (1954); transl. RUBBER CHEM. & TECHNOL. **30**, 548–54 (1957).

[2] Dogadkin, B. A., Feldshteĭn, M. S. and Pevzner, D. M., in "Vulkanizatsiya Rezin" (Conference, June 1953), p. 7 (similar paper from *Zhur Prikl. Khim.* **28**, 533–42 (1955), available as RABRM Transl. 477).

[3] 'Prochnost' Svyazi...(Conference, Dec. 1954), p. 87 (RABRM Transl. 681), p. 118 (RABRM Transl. 700), p. 151.

[4] Malzel's, M. G. and Raevskiĭ, V. G., *Kauch. i Rezina*, **1960**, No. 1, 16; translated in corresponding issue of *Soviet Rubber Technol.*, p. 16.

[5] Voyutskiĭ, S. S. *et al.*, *Kolloid Zhur.* **19**, 274 (1957); transl. in RUBBER CHEM. & TECHNOL. **31**, 712–8 (1958).

[6] Voyutskiĭ, S. S. and Vakula, V. L., *Vys. Soed.* **2**, No. 1, 51 (1960).

[7] Kargin, V. A. *et al.*, *Doklady Akad. Nauk SSSR* ,**130** No. 2, 356 (1960).

[8] Liang, C. Y. and Marchessault, R. H., *J. Polymer Sci.* **35**, No. 129, 529 (1959).

[9] Kargin, V. A., *Vys. Soed.* **2**, No. 3, 466 (1960).

STRESS AS A REDUCED VARIABLE: STRESS RELAXATION OF SBR RUBBER AT LARGE STRAINS *

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INTRODUCTION

The reduced variable concept for linear viscoelastic behavior covering the effects of time, temperature, and concentration (for solutions) proposed by Ferry[1] ten years ago has proven to be eminently successful as a method of showing the interactions between these parameters and of correlating data obtained over wide ranges in them[2]. In principle this treatment is limited to deformation sufficiently small for an isochronal stress-strain relationship to be considered linear. Nevertheless, it has been found that ultimate properties have the same time and temperature interdependence as small deformation properties[3, 4]. Therefore, one would like to be able to extend the reduced variable treatment to the nonlinear region, i.e., to larger deformations. A most promising start in this direction has been reported by Mason[5] since the inception of this work. We report these results on the basis of a somewhat different outlook on the same problem and an extension to even higher strains.

Linear behavior is here taken to represent behavior which can be described in terms of an array of Hookean springs and Newtonian dashpots. The total response of the array may not be linear in that the stress may not be proportional to the strain or rate of strain, particularly under dynamic conditions, but that of the individual elements is. Extension to nonlinear elements is possible, but leads to mathematical difficulties which are not easily solved[6,7]. The restriction to linearity is now examined and a method of circumventing it is proposed.

The most general expression of the tensile stress-strain law simply states that the stress based on the initial cross-sectional area S is proportional to the strain e through some function f of time t, absolute temperature T, and strain e or extension ratio $\alpha(= e + 1)$.

$$S = ef(t,T,\alpha) \tag{1}$$

For small deformations the effects of time and temperature are factorable, though interrelated through the Ferry shift factor a_T. Thus Eq. (1) can be rewritten as

$$S = ef(\alpha)g(T)h(t/a_T) \tag{2}$$

where for small deformations $f(\alpha)$ is unity and $g(T)h(t/a_T)$ is the time- and temperature-dependent Young's modulus $E(T,t/a_T)$. The latter is directly

* Reprinted from *Journal of Applied Physics*, Vol. 31, 1885–1891 (1960). This is JPL Technical Report No. 32-11 based on work done under National Aeronautics and Space Administration Contract No. NASw-6.

proportional to T, so $g(T)$ is simply T and $h(t/a_T)$ equals $T^{-1}E(t/a_T)$. But if the effects of large strains are also factorable, then at any given temperature there results a modified Hooke's law

$$S = E(t)ef(\alpha) \tag{3}$$

Therefore this equation can be linearized by defining a strain-reduced stress S^* as $S/f(\alpha)$ and the resulting expression can be used in the standard equations for viscoelastic behavior derived for spring-dashpot arrays. This factorization is tacitly assumed but not explicitly demonstrated by Mason[5].

What we propose to try, then, is to choose the proper form of $f(\alpha)$ in order to be able to calculate S^*, and then employ this reduced-stress, stress-strain curve in subsequent calculations. Therefore, as a first step in this process the various proposed forms of $f(\alpha)$ must be evaluated to see which expression will most adequately describe experimental results and so give the required analytic representation. Note, however, that this evaluation must be carried out at constant $E(t)$. This can be done in one of two ways: either by making stress relaxation or creep measurements and considering isochronal data, or by making actual stress-strain measurements at such high temperatures and low strain rates that $E(t)$ will be at its equilibrium value and constant throughout the course of the experiment.

One of the first difficulties encountered in attempting to describe nonlinear viscoelastic systems is the requirement of a suitable analytic representation of the stress-strain curve of a rubber. Although there have been a large number of equations proposed for this purpose, few are adequate over wide ranges in experimental test conditions.

In general, the proposed stress-strain equations can be subdivided into two categories, theoretical and empirical or semiempirical. In the former class we may list the modified Hooke's law, the kinetic theory expression[8], and the Mooney-Rivlin expression[9, 10]. The modified Hooke's law,

$$\alpha S = E(t)e \tag{4}$$

can be justified on the assumption that Poisson's ratio is one-half, and so the measured stress should be corrected to a true stress by the factor α. The more fundamentally significant kinetic theory expression

$$S = \frac{E(t)}{3}\left(\alpha - \frac{1}{\alpha^2}\right) \tag{5}$$

is nonlinear, but on multiplying through by the quantity α and expanding $\alpha^2 - 1/\alpha$ in a power series, an equation analogous to Eq. (4) is obtained which is approximately linear to 50% strain. This observed linearity can also be offered in support of the use of Eq. (4). A more recent improvement on the kinetic theory is the Mooney-Rivlin expression

$$S = \frac{E(t)}{6}\left(\alpha - \frac{1}{\alpha^2}\right) + 2C_2\left(1 - \frac{1}{\alpha^3}\right) \tag{6}$$

where C_2 is an additional time dependent constant which should go to zero at truly equilibrium test conditions for a well crosslinked network[11].

Of the empirical or semiempirical equations, we should like to mention only two—that proposed by Blanchard and Parkinson[12]:

$$S = E(t)\left(\frac{1}{\alpha} - \frac{1}{\alpha^2}\right)\exp B(\alpha - 1) \tag{7}$$

and a purely empirical expression discovered by Martin, Roth, and Stiehler (MRS)[13]:

$$S = E(t)\left(\frac{1}{\alpha} - \frac{1}{\alpha^2}\right)\exp A\left(\alpha - \frac{1}{\alpha}\right) \tag{8}$$

Equation (8) was devised as a curve-fitting scheme for isochronal stress-strain data obtained from creep curves by replotting the strain increments observed at a given time. One of the more interesting conclusions of this study was the fact that the parameter A had a nearly constant value of 0.38 for all the rubbers studied: natural, butyl, styrene-butadiene, and nitrile.

In a separate study on the actual stress-strain behavior at high temperatures and low strain rates of a polyurethane rubber, and from SBR data of Smith[4], it has been found that of all the suggested equations only the MRS equation, Eq. (8), adequately describes the behavior. Moreover, it does so over the

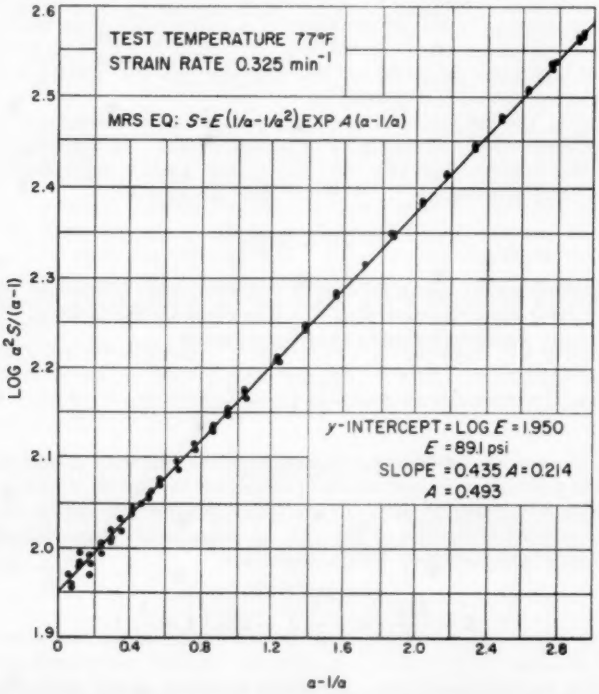

FIG. 1.—Stress-strain data for a polyurethane elastomer, plotted as suggested by Eq. (9).

whole stress-strain curve, right out to the breaking strain. It is surprising to us that so simple an expression—it really contains only two arbitrary parameters—can describe the stress behavior over the complete range of strain. Since Eq. (8) can be rearranged to

$$\log (\alpha^2 S/e) = \log E(t) + 0.434\, A(\alpha - 1/\alpha) \tag{9}$$

a plot of $\log \alpha^2 S/e$ vs. $\alpha - 1/\alpha$ should be linear with the slope 0.434 A, provided $E(t)$ is constant.

As an illustration, Figure 1 shows such a plot for three samples of polyurethane tested as ring-shaped specimens. The breaking strain in this case was 225%. The plot is linear as required and $E(t)$ is found to have essentially

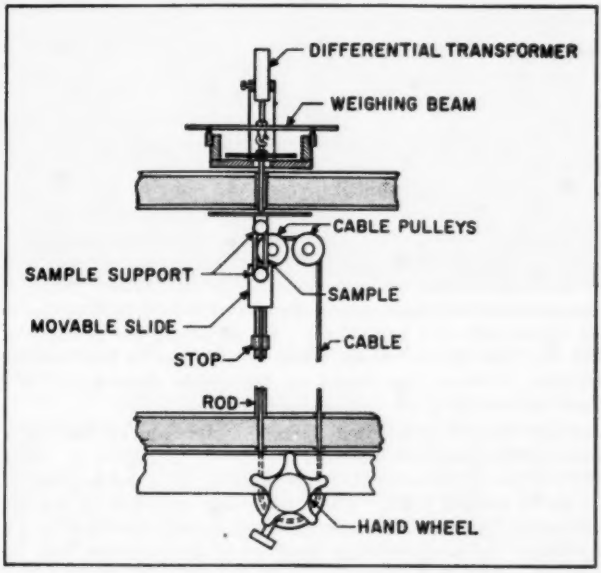

FIG. 2.—Sketch of the stress-relaxometer.

the same value as found from the use of Eqs. (4) and (5) on the same data at smaller strains. However, these experiments indicated a value of A which, though reasonably constant for a given rubber, varied between 0.4 and 0.5. This is in contrast to the reported value of 0.38. On the other hand, the experiments may not have been carried out under conditions sufficiently close to equilibrium, so that $E(t)$ may not have been constant as assumed. Therefore it became imperative to test the expression on isochronal data.

Such data were obtained as stress relaxation moduli measured during the course of a study whose primary aim was simply to examine the influence of strain on the time to rupture[15]. The present work was included as a corollary to test the MRS equation as indicated above and to provide data for an experimental test of the reduced variable concept.

EXPERIMENTAL

The styrene-butadiene rubber was obtained from the National Bureau of Standards. It contains 23.5% styrene and has an average molecular weight between crosslinks of 15,800, as determined by swelling experiments in several solvents. A more complete description is given in Ref. 15.

The test specimens were rings cut from the rubber sheets with a circular die having an inside diameter of 1.400 inches and an outside diameter of 1.650 inches. The outer cut edges of the rings were always slightly concave. This slight imperfection was disregarded in calculating the cross-sectional area of the samples, and the directly observed width as measured with a micrometer was employed. The ring dimensions were 0.078 (+0.002, −0.003) in. thick by 0.125 (+0.004, −0.003) in. wide, the indicated deviations being the maximum observed. In any given run the average dimension for all samples employed in that run was used in calculating the stress.

The stress relaxometer was a specially constructed apparatus shown in Figure 2. The load cell was a simply supported beam whose motion under load was detected by a linear variable differential transformer. A Wiancko carrier system provided a stable 1000 cps excitation signal and rectified the transformer output so that the latter could be recorded with a standard recorder. The load cell was calibrated before each run by suspending a series of known weights from the beam and recording the transformer signal. The output was a linear function of the applied force, within about 1%. A small, freely rotating nylon pulley was supported from the center of the beam and a matching pulley was mounted on a slide movable along a brass rod by means of a cable and handwheel located outside the apparatus. Ring specimens could be looped over both pulleys and then extended by pulling the slide down the desired extent with the handwheel. By adjusting the position of a metal stop on the rod, the desired strain could be attained in two seconds or less. The calculation of strain was based on the inside diameter D of the ring, $e = 2\Delta C/\pi D$, where ΔC is the pulley displacement.

An assembly of eight of these stress relaxometers was enclosed in a circulating-air, constant-temperature chamber as shown in Figure 3. Heating was provided by a series of nichrome elements; cooling, by a mechanical refrigerator unit and a set of cooling coils. These units are mounted on the back of the chamber shown in Figure 3. Temperature control was provided by a bimetallic thermoregulator. At temperatures near room temperature and below, the refrigerator was allowed to run continuously and the requisite amount of balancing heat was provided by the heaters. The maximum temperature spread between various points within the chamber was about 1° C. At any given point the temperature was constant within ±0.5° C over many hours, but only to within about 1.5° C over a period of days. During a test, it was necessary to bleed a stream of dry nitrogen continuously into the system to prevent condensation on the refrigerated cooling coils, because even slight condensation interfered sufficiently with the heat transfer rate to prevent the system from operating at a stable temperature. The nitrogen was also intended to reduce the possibility of oxygen and ozone attack on the stretched SBR specimens. However, a mass spectrographic analysis of the air withdrawn from the chamber showed that the oxygen content had been reduced to only about 7%, so this purpose was not fulfilled. Ozone cannot be detected as such by the mass spectrometer, since it reacts in the spectrometer to form oxygen.

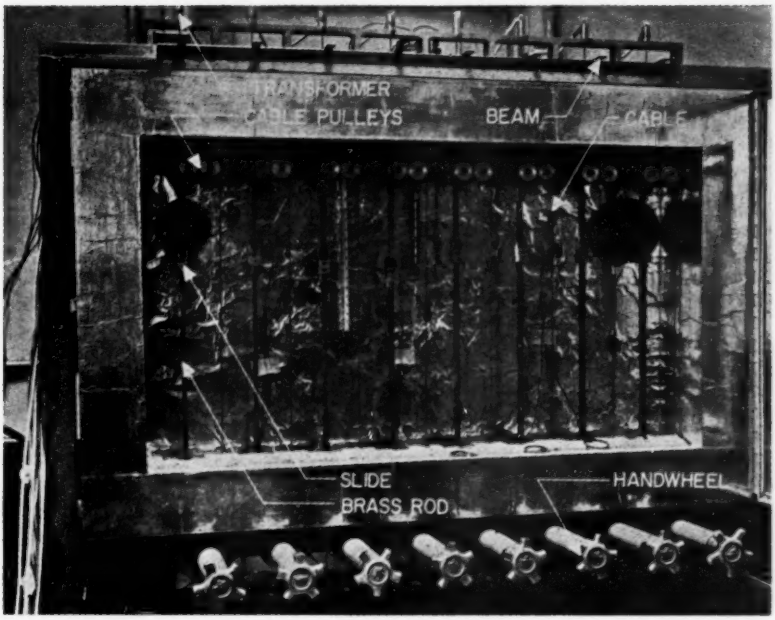

FIG. 3.—Over-all view of the stress relaxometer and the air thermostat.

We are indebted to Dr. William DeMore of this Laboratory for making these measurements.

The over-all accuracy of the results is limited by several factors: sample-to-sample variability; the ability to measure the sample dimensions accurately; the variation in strain rate employed during the initial elongation; the sensitivity and drift of the load-measuring system, including the recorder; and temperature fluctuation. The first three factors affect the accuracy; the remainder, the precision. The most important factors are the apparatus sensitivity and, particularly at lower temperatures, the differences in the rate at which the initial strain is applied. For any given stress relaxation experiment, the precision is estimated to be ±5%, while the over-all accuracy at any given temperature is estimated to be ±10–20%.

TABLE I

INITIAL STRAINS APPLIED AT THE VARIOUS TEMPERATURES

Temperature, ° C	Strain range[a], %
−5.0	275–550
1.7	325–525
7.2	325–525
12.8	200–500
18.3	150–450
40.0	100–350
50.0	50–300
60.0	50–300

[a] The strains were varied in 25% increments over this range.

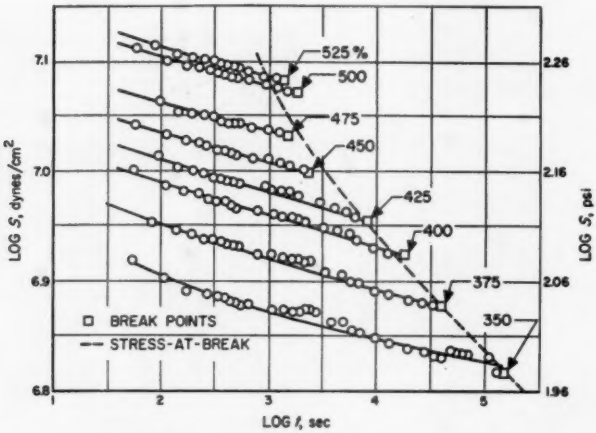

FIG. 4.—Stress relaxation to break in SBR under large strains at 1.7° C. The figures indicate the % strain initially applied.

The experiments were carried out at ten temperatures between −15 and +60° C and at several strains between 50 and 550%, as indicated in Table I. The results at −15 and +29.4° C are omitted from subsequent discussion in this paper because the reduced modulus data are inconsistent with the data at other temperatures.

In addition, a limited number of constant strain rate tensile tests were made in order to apply the MRS equation to tensile data for this same rubber, both to obtain a value of A by this method for comparison with that obtained

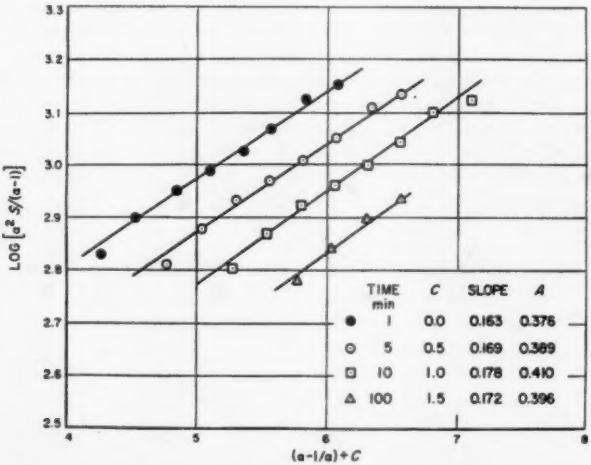

FIG. 5.—Data of Figure 4 cross-plotted as indicated by Eq. (9) to find A of the MRS equation.

TABLE II

CONSTANT A IN MRS EQUATION

Temperature °C	S_1	S_5	S_{10}	S_{100}	S_{1000}	$S_{10,000}$	Average
−5.0	0.40	0.42	0.42	0.42	0.43	0.45	0.42
1.7	0.38	0.39	0.41	0.40	—	—	0.39
7.2	0.40	0.41	0.40	0.41	0.39	0.39	0.40
12.8	0.35	0.35	0.36	0.36	0.37	0.37	0.36
18.3	0.39	0.40	0.40	0.41	0.43	0.44	0.41
40.0	—	0.43	0.43	0.44	—	—	0.43
50.0	—	0.40	0.40	0.39	0.44	—	0.41
60.0	—	0.42	0.43	0.42	0.46	—	0.42
Average	0.38	0.41	0.41	0.41	0.42	0.41	0.40
							0.41

from isochronal data, and also to be able to construct a reduced stress-strain curve in the manner of Smith[16]. The latter is important because $E(t)$ can be calculated from such a curve and should serve as a basis of comparison with $E(t)$ obtained directly from the stress relaxation data.

RESULTS AND DISCUSSION

Determination of the MRS constant A.—Typical stress relaxation curves are shown in Figure 4. The constant A can be evaluated from these data by interpolating the stress values at times of 1, 5, 10, and 100 minutes and cross-plotting as indicated by Eq. (9). The results for the curves of Figure 4 are shown in Figure 5, and the value of A thus obtained is given in the figure. The value of A cannot be determined with precision.

The results for the determination of A at all temperatures are given in Table II. It can be seen that there is a slight dependence of A on both the temperature and on the time at which readings are taken. Figure 6 compares the temperature dependence of the average value of A given in Table II with that obtained in the constant strain rate experiments. Although the data, when taken together, apparently indicate a uniform increase with temperature at a rate somewhat less than directly proportional to the absolute temperature, the constant strain rate data are suspect at lower temperatures because of the assumption of equilibrium behavior and the constancy of $E(t)$. If log $E(t)$,

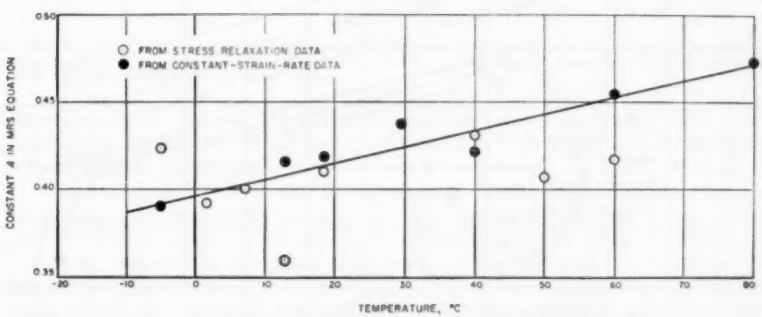

FIG. 6.—Temperature dependence of the average value of A of Table II and the value found in constant strain rate experiments.

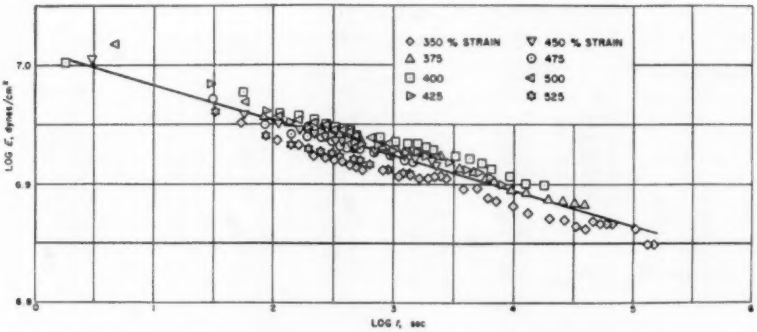

FIG. 7.—Strain-reduced stress relaxation modulus calculated from the data of Figure 4.

the intercept of plots such as Figure 1, is decreasing while the stress-strain curve is being measured, then the effect will be to decrease the apparent value of A with decreasing temperature, as observed. The values obtained in the stress relaxation experiments do not suffer from such a defect, but on the other hand, the experimental scatter is so great that one cannot decide whether or not A is temperature dependent.

The average values of A, at each temperature, also show a consistent increase with log time. If true, this would represent a serious drawback to the utility of the MRS equation. However, in view of the experimental error in determining A (see Figure 5), it seems reasonable to use an average value of 0.40 for subsequent calculations.

Reduced variable treatment in terms of strain-reduced stress.—Assuming that the required function of α is given by the MRS equation, and taking the value

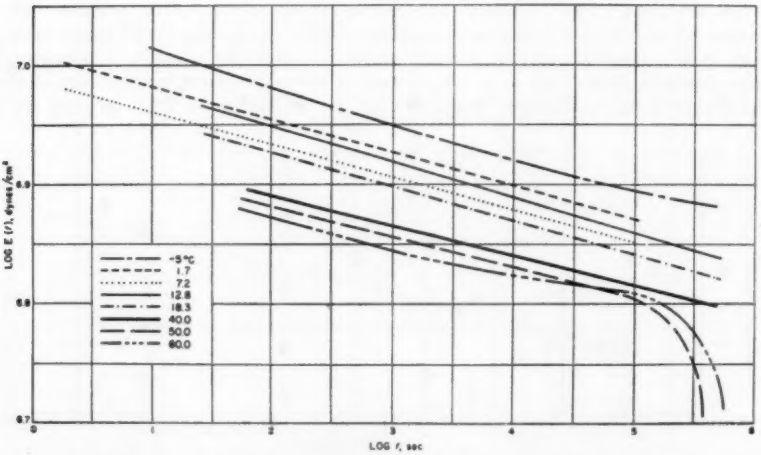

FIG. 8.—Strain-reduced stress relaxation modulus of SBR at temperatures from −5 to +60° C. The initial strains range from 50 to 550%, as indicated in Table I.

of A to be 0.40, the expression for the strain-reduced stress relaxation modulus is given by

$$E(t) = \frac{S^*}{e} = \frac{\alpha^2 S}{e} \exp\left[-0.40\left(\alpha - \frac{1}{\alpha}\right)\right] \tag{10}$$

Figure 7 shows the results using the data of Figure 4. The family of stress relaxation curves shown there has been compressed to a single modulus curve within experimental error. The latter shows up all too clearly on a plot to this scale. Nevertheless, one may draw an average curve through the results at all six strains. Figure 8 shows this average curve and the corresponding curves for other temperatures. The curve at 12.8° C seems to contain a

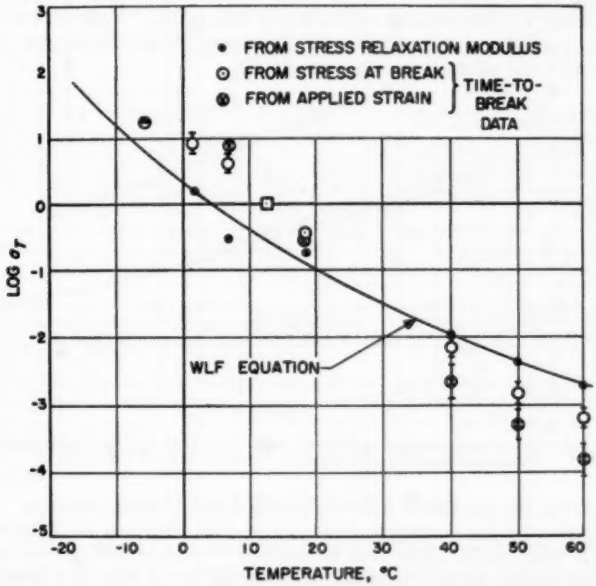

FIG. 9.—Log a_T determined from superposing the data of Figure 8. Also shown are a_T values obtainen from the ultimate property and time-to-break data of Ref. 14. The square shows that 12.8° C was chosed as the reference temperature for superposition.

systematic error, since it is too high relative to the other curves. The sharp drop in log $E(t)$ at 10^5 to 10^6 sec at 50° and 60° C is attributed to oxidative degradation of the rubber.

These averaged curves can be superposed in the normal fashion by first converting the measured modulus to the reduced modulus[2] $E_r(t) = E(t)$ 286° K/T and then subjecting these reduced modulus plots to a suitable horizontal translation along the time scale. The extent of the translation is defined as $1/a_T$. Values of a_T so obtained, as well as values from the time-to-break data[14], are shown in Figure 9, where they are compared with the values predicted by the WLF equation[16]. As originally defined[2], $E_r(t) = E(t)T_0\rho_0/T\rho$, where ρ is the corresponding density. The small density correction has been

omitted in these calculations.

$$\log a_T = \frac{-17.44(T - T_g)}{51.6 + T - T_g} \tag{11}$$

where T_g is the glass transition temperature. The agreement is rather good for the modulus data, but poor for the points from ultimate property data. The latter show a much greater dependence on T than does the WLF function. Since the reason for this discrepancy has not yet been established, the WLF curve is drawn for a best fit to the modulus results. T_g is estimated by this procedure to be $-55°$ C, vs. an experimental determination of $-59°$ C based on linear thermal expansion measurements.

Average log a_T values were read from Figure 9 and used to superpose the data of Figure 8. The results are shown in Figure 10. Note that the sharply decreasing portions of the 50° and 60° C curves do not superpose, as indeed they cannot if the effect is due to degradation.

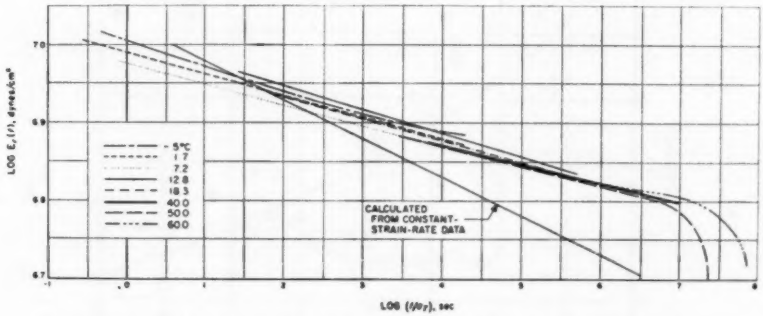

FIG. 10.—Superposed strain-reduced modulus for SBR, T_0 = 12.8° C. Also shown are the results calculated from the constant strain-rate data of Figure 11.

The curves are too flat to afford a positive test of superposition. A better test is afforded by the comparison of moduli data obtained at different ranges of the real time scale. For this purpose we compare the stress relaxation modulus calculated from a reduced stress-strain curve with the more directly measured results of Figure 10.

The stress-strain data can be superposed in the original manner of Smith[16] to give a composite stress-strain curve by simply plotting log $\alpha ST/T_0Ra_T$ vs. log e/Ra_T, where R is the strain rate. Thus the reduced stress is αS and $f(\alpha) = \alpha^{-1}$. Figure 11A shows the results for such a superposition using a_T values calculated from Eq. (11), with $T_g = 59°$ C. The individual stress-strain curves are concave upward and their initial portions define the envelope of all of the curves, as previously noted by Smith. In the present instance the envelope is essentially a straight line over this region of the reduced time scale.

The MRS equation can similarly be used to reduce the data, except of course that the reduced stress is that indicated in Eq. (10). The superposed plot thus obtained is shown in Figure 11B. The MRS function has now converted all of the stress-strain curves into straight line segments, and practically all of the points now lie on a single line. This line is, of course, the same as the

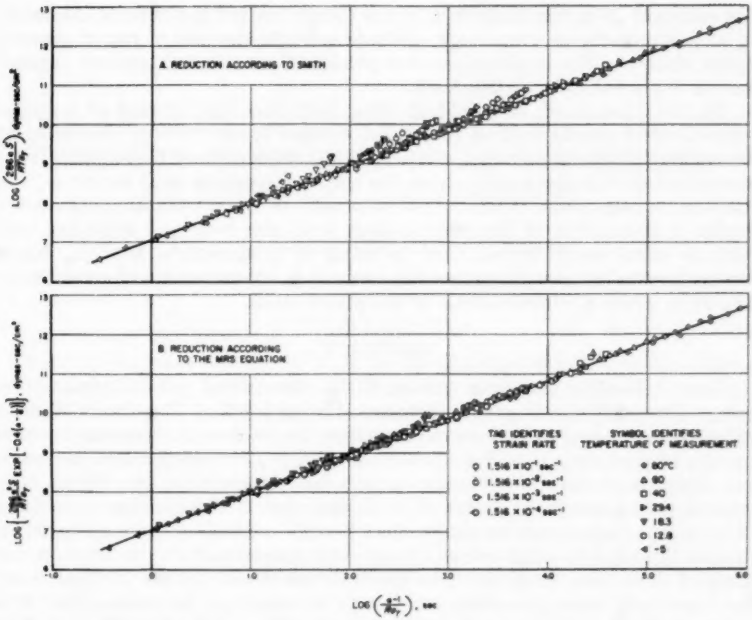

FIG. 11.—Stress-strain data on SBR at various temperatures and strain rates, reduced to a composite stress-strain curve at 12.8° C. A. Reduction according to Smith[11], $f(\alpha) = \alpha^{-1}$; B. Reduction according to the MRS equation, $f(\alpha)$ given by Eq. (10).

envelope in Fig. 11A, since at low strains the results become independent of the reduced stress employed. The stress relaxation modulus $E(t)$ can be obtained from the slope of either of these plots at any desired value of reduced time $t_r = e/Ra_T$, as

$$E(t) = (S^*/t_r)(d \log S^*/d \log t_r) \tag{12}$$

If the use of the reduced stress concept and the MRS equation is correct, then these values of the stress relaxation modulus should fall on the superposed curve of Figure 10. Instead, the results cross over and fall progressively below the superposed curves. However, when it is considered that the maximum discrepancy between the two results is 0.1 log unit, no more than the diameter of the data points shown in Figure 11, the agreement can be considered very satisfactory.

CONCLUSIONS

Since the experimental data obtained at quite different times, temperatures, and strains showed reasonable agreement, it may be concluded that the concept of strain-reduced stress as a reduced variable is generally valid. Thus Ferry's method of reduced variables may be extended to large deformations by employing a strain-reduced modulus $E(t)f(\alpha)$ where $f(\alpha)$ is an appropriate function of the strain. Such a function was obtained from the Martin-Roth-Stiehler equation, but the validity of its use in this reduction was not definitely established.

The constant A in the MRS equation is clearly related to the finite extensibility of polymer chains, since its magnitude controls the rate of rise of stress at higher strains. The implications of a possible time and temperature dependence of A are not clear at this time.

On the other hand, it should be recognized that this concept of a strain-reduced stress cannot hold at very short reduced times. Ferry[17] has recently shown that if strain produces a free volume change, then there will exist a time-strain shift factor analogous to the time-temperature shift factor a_T. In this case, superposition of isothermal data such as stress relaxation curves will require a translation of the curves along both the time and modulus axes. Such an effect would be expected to occur at temperatures near T_g, where Poisson's ratio is decreasing from the value of $\frac{1}{2}$, characteristic of a rubber, to a value of about $\frac{1}{3}$, characteristic of the glassy state.

ABSTRACT

Stress relaxation measurements on SBR were carried out at temperatures from -5 to $+60°$ C and at initial strains of up to 550%. The effects of strain and time were found to be factorable, so that the isochronal stress-strain curve may be written as a modified Hooke's law with a time-dependent modulus: $S = E(t)ef(\alpha)$, where $f(\alpha)$ is an appropriate function of the strain. By defining a strain-reduced stress $S^* = S/f(\alpha)$, i.e., a strain-reduced modulus $E^*(t) = E(t)f(\alpha)$, it can be shown that Ferry's method of reduced variables may be extended to large deformations. An appropriate strain function was obtained from the empirical Martin-Roth-Stiehler equation as $f(\alpha) = \alpha^{-2} \exp A(\alpha - \alpha^{-1})$ with $A = 0.40$. Although it cannot yet be certain that A is truly a constant and the same for all elastomers, this equation has the advantage of being valid right out to the breaking strain.

REFERENCES

[1] Ferry, J. D., *J. of the Am. Chem. Soc.* **72**, 3746 (1950).
[2] For a recent summary discussion of the reduced variable treatment see *Die Physik der Hochpolymeren*, ed. by H. A. Stuart, Springer-Verlag, Berlin, 1956, especially page 56 et seq. in chapter 1, by A. J. Staverman and F. Schwarzl, and chapter 6, by J. D. Ferry.
[3] Bueche, F., *J. Appl. Phys.* **26**, 1133 (1955).
[4] Smith, T. L., *J. Polymer Sci.* **32**, 99 (1958).
[5] Mason, P., *Trans. Faraday Soc.* **55**, 1461 (1959); *J. Appl. Polymer Sci.* **1**, 63 (1959).
[6] Green, M. S. and Tobolsky, A. V., *J. Chem. Phys.* **14**, 80 (1946).
[7] Blatz, P. J. and Tobolsky, A. V., *J. Chem. Phys.* **14**, 113 (1946).
[8] Flory, P. J., *Principles of Polymer Chemistry*, Ithaca, New York, Cornell University Press, 1953.
[9] Mooney, M., *J. Appl. Phys.* **11**, 582 (1940).
[10] Rivlin, R. S. and Saunders, D. W., *Phil. Trans. Royal Soc.* (London) Series A, Mathematical and Physical Science **243**, 251 (1951).
[11] Ciferri, A. and Flory, P. J., *J. Appl. Phys.* **30**, 1498 (1959).
[12] Blanchard, A. F. and Parkinson, D., *Ind. Eng. Chem.* **44**, 799 (1952).
[13] Martin, G. M., Roth, F. L. and Stiehler, R. D., *Trans. Inst. Rubber Ind.* **32**, 189 (1956); Rubber Chem. & Technol. **30**, 876 (1957).
[14] Unpublished experiments of R. F. Landel, P. J. Stedry and T. L. Smith.
[15] Smith, T. L. and Stedry, P. J., *J. Appl. Phys.* **31**, 1892 (1960); following paper, this issue.
[16] Smith, T. L., *J. Polymer Sci.* **20**, 89 (1956).
[17] Williams, M. L., Landel, R. F. and Ferry, J. D., *J. Am. Chem. Soc.* **77**, 3701 (1955).
[18] Ferry, J. D. and Stratton, R. A., *Kolloid Z.* **171**, 107–111 (1960).

TIME AND TEMPERATURE DEPENDENCE OF THE ULTIMATE PROPERTIES OF AN SBR RUBBER AT CONSTANT ELONGATIONS *

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I. INTRODUCTION

A study was made previously of the temperature and strain rate dependence of the stress at break (tensile strength) and the ultimate elongation of an unfilled SBR rubber[1]. In that study, stress-strain curves to the point of rupture were measured with an Instron tensile tester on ring type specimens at 14 temperatures between $-67.8°$ and $93.3°$ C, and at 11 strain rates between 0.158×10^{-3} and 0.158 sec^{-1} at most temperatures. The tensile strength was found to increase with both increasing strain rate and decreasing temperature. At all temperatures above $-34.4°$ C, the ultimate elongation was likewise found to increase with increasing strain rate and decreasing temperature but at lower temperatures the opposite dependence on rate was observed; at $-34.4°$ C, the ultimate elongation passed through a maximum with increasing rate.

Values of the ultimate properties at each temperature were plotted against log $1/R$, where R is the strain rate. The resulting curves were then superposed by shifting them along the log $1/R$ axis, the shift distance required to effect superposition being log a_T. Values of log a_T obtained from superposing the tensile strength data were equal, within experimental error, to those obtained from superposing the ultimate elongation data. Further, these values of log a_T were found to fit the Williams, Landel, and Ferry (WLF) equation[2]

$$\log a_T = -\frac{8.86(T - T_s)}{101.6 + T - T_s} \tag{1}$$

with the standard reference temperature T_s equal to 263° K. In this form of the WLF equation, T_s is normally about 50° C above the glass temperature T_g of a material. Thus, the value obtained for T_s indicated T_g should be 213° K, in close agreement with 210° K obtained from dilatometric measurements. Values of a_T given by Eq. (1) were used to construct two reduced curves which showed all ultimate property data plotted against log $1/Ra_T$. These curves showed the strain rate dependence of the tensile strength and the ultimate elongation, over many decades, at the standard reference temperature.

In studying the linear viscoelastic properties of amorphous polymers above T_g, many workers have found the shift factor a_T to be extremely useful for interconverting the effects of temperature and experimental time scale. The

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conclusion from the study of the SBR rubber was that a_T can also be used to interconvert the effects of temperature and strain rate on the ultimate properties of certain types of polymeric materials. Prior to this work, F. Bueche[3] presented a theory which predicted that values of the tensile strength measured at different temperatures and under either constant loads or strain rates can be interrelated by using a_T values. To check the theory, Bueche measured the tensile strength of polybutyl methacrylate under constant loads at temperatures above T_g and applied time-temperature superposition to reduce the data to a single temperature.

The shift factor is given by the relation $a_T = (T_0/T) \times (\eta/\eta_0)$, where η is the viscosity (or internal viscosity for crosslinked polymers) at temperature T and η_0 is the viscosity at some arbitrary reference temperature T_0. Because T_0/T differs from unity by a relatively small amount, a_T equals approximately the viscosity ratio η/η_0, and consequently the temperature dependence of a_T is essentially the same as that of the viscosity. Thus, the observation that a_T can be used to interconvert the effects of strain rate and temperature on the ultimate properties—at least for materials like SBR rubber—leads to the following conclusions: (1) The ultimate properties vary with temperature because the internal viscosity varies with temperature; (2) the ultimate properties vary with strain rate because the viscous resistance to network deformations increases with the rate; and (3) the temperature dependence of factors such as the rate of bond rupture have no significant effect on the temperature dependence of the ultimate properties.

Values of the ultimate properties shown by the reduced curves in a previous paper[1] have now been replotted in Figure 1 against the time to break (t_b) expressed in seconds and reduced to 263° K; t_b equals γ_b/Ra_T where γ_b is the strain at break measured at a strain rate R and temperature T, and S_b is the stress at break based on the initial cross-sectional area of the specimen. Figure 1 shows that the ultimate properties become relatively insensitive to strain rate at sufficiently low rates; the shapes of the curves suggest that asymptotes may exist which have near-zero slopes. Because of kinetic effects which must be associated with the chain scissions which lead to specimen rupture, it is un-

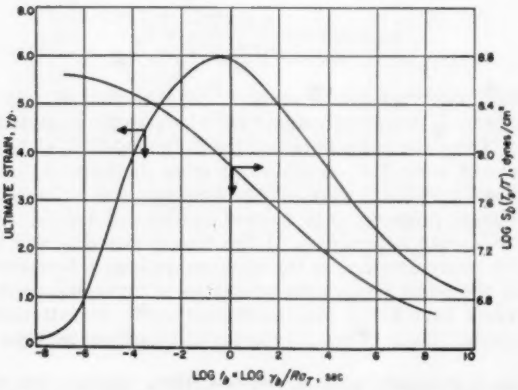

FIG. 1.—Ultimate properties of an SBR rubber measured at different strain rates and temperatures. Data plotted against the logarithm of the time to break (t_b) reduced to −10° C. (Data from work cited in footnote 1.)

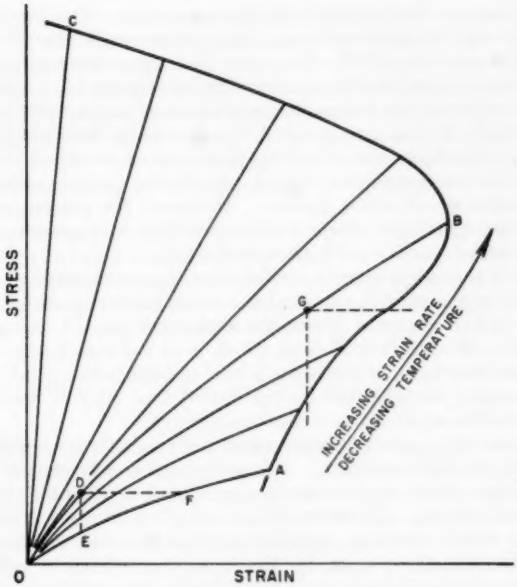

FIG. 2.—Schematic representation of the variation of stress-strain curves with strain rate and temperature. Envelope connects rupture points and the dotted lines illustrate stress relaxation and creep under different conditions.

likely that asymptotes of zero slope exist. However, the asymptotic or long-time values of the ultimate properties are of major significance because such values are nearly independent of the testing conditions and are characteristic of the network in the absence of viscous effects.

An important qualitative conclusion above the time-dependent ultimate properties can be reached by examining Figure 1. For example, this figure shows that a specimen will break at 300% elongation provided the strain rate is selected so that 10^5 sec are required to reach this elongation. Let us suppose, however, that a specimen is stretched at the strain rate needed to produce a 300% elongation in 100 sec and that the elongation is subsequently held constant. Immediately after the sample is stretched, the stress will begin to relax because the sample was not stretched under equilibrium conditions. Although the stress decays, the sample will break eventually because it can withstand an elongation of only about 100% when the network chains are in an equilibrium condition. As a rough approximation, it might be expected that the sample will break after a total of 10^5 sec, as indicated by the curve which shows the ultimate strain plotted against log t_b. However, this curve represents data measured under conditions of constant strain rate, and it is to be expected that values of the ultimate properties, like other time-dependent mechanical properties, will depend on the path.

Important conclusions about the time dependence of the ultimate properties can also be reached by considering the diagram in Figure 2. This diagram shows schematically stress-strain curves, including the rupture points,

measured at various strain rates and temperatures. The variation of the stress at break and the strain at break with either strain rate or temperature is shown by the envelope *ABC*. The curve *OA* represents equilibrium stress-strain conditions, except possibly in the vicinity of point *A*. Although curve *OA* represents stress-strain values in the absence of viscous effects, true equilibrium—especially in the vicinity of *A*—undoubtedly does not exist because under suitable conditions stress leads to breakage of chemical bonds. Thus, values of the ultimate properties are not expected to be unique but to depend on the temperature and stress history. However, for present purposes, we can ignore such degradation effects and assume that *A* represents the ultimate properties measured under equilibrium conditions.

Suppose now that a specimen is stretched at the strain rate and temperature required to traverse curve *OB*, and that the strain is held constant after point *D* is reached. At the constant strain the stress relaxes, as indicated by the dotted vertical line, until it reaches *E*, which is on the equilibrium stress-strain curve. On the other hand, if the stress is held constant after point *D* is reached, the strain increases, as indicated by the dotted line, until it reaches point *F*, which is also on the equilibrium stress-strain curve.

Next suppose that curve *OB* is traversed until point *G* is reached and thereafter the strain is held constant. The stress again relaxes, but because no equilibrium stress exists for the strain represented by point *G*, the specimen should eventually break. Likewise, if the stress is held constant after point *G* is reached, the strain increases, and the specimen should eventually break because no equilibrium strain exists for the stress represented by point *G*.

Studies have been made of the time to break for various materials under constant loads[4], although with several possible exceptions[3,5] most studies have been made of rigid materials. Apparently, no studies have been made of ultimate properties under constant strain conditions. Thus, the primary purpose of the present work was to obtain experimental confirmation of the prediction that certain rubbers when held at constant elongation will rupture eventually, provided the elongation exceeds some critical value; the secondary purpose was to see how values for the ultimate elongation and stress at break, measured under constant strain conditions, compare with values measured under constant strain-rate conditions. Because tensile strength is usually defined as the maximum stress developed during certain types of tests, it seems desirable here to speak of the stress at break, and to call the stress at break the tensile strength only when it equals the maximum stress developed during a test. To obtain the desired data, measurements were made at various temperatures of the stress-relaxation of an SBR rubber under relatively large elongations; the apparatus used and the stress-relaxation data obtained are discussed in detail elsewhere[6]. This paper presents data on the time required for the rupture of specimens subjected to various elongations at various temperatures and the stress existing at the time of rupture. For comparative purposes, a limited study was also made of the ultimate properties of the SBR rubber at different strain rates and temperatures.

II. EXPERIMENTAL

MATERIAL

Ultimate properties were measured of a gum vulcanizate of a styrene-butadiene rubber (SBR) which was supplied in the form of ASTM tensile sheets (*ca.* 0.080 in. thick) by the Rubber Section of the National Bureau

of Standards. The base polymer was NBS reference sample 387 (X-768), which contained 23.5% bound styrene and had been prepared by emulsion polymerization at 50° C. The gum vulcanizate, which was cured for 60 min at 150° C, contained the following parts by weight: SBR, 100 parts; zinc oxide, 5 parts; sulfur, 2 parts; benzothiazyl disulfide, 1.75 parts. The sheets of the vulcanizate were stored in a freezer prior to being used. The vulcanizate used in the previous study[1] was the same except that 1 part of mercaptobenzothiazole was used in place of 1.75 parts of benzothiazyl disulfide and cure was for 45 instead of 60 min.

The average molecular weight between crosslinks M_c for the vulcanizate was determined from swelling measurements in four solvents. Duplicate weighed pieces of SBR were immersed in the solvents for four days at 25° C, and the swollen samples were weighed after removing excess solvent from their surfaces with filter paper. Values of M_c were calculated using the equation

$$\ln (1 - v_2) + v_2 + \chi_1 v_2^2 = -\rho \frac{V_1}{M_c}\left(v_2^{\frac{1}{3}} - \frac{v_2}{2}\right)$$

where v_2 is the volume fraction of polymer in the swollen gel, ρ is the density of SBR, V_1 the molar volume of the solvent, and χ_1 the solvent-polymer interaction parameter. Values of χ_1, approximated as described previously[1], are given in Table I along with the values of M_c for both the present vulcanizate and the vulcanizate used in the previous study.

TABLE I

VALUES OF M_c FROM EQUILIBRIUM SWELLING DATA

Solvent	χ_1	Previous vulcanizate	Present vulcanizate
Carbon tetrachloride	0.300	8000	15,957
Xylene	0.305	8657	16,647
Toluene	0.316	8000	15,998
Benzene	0.345	7424	14,802
		av 8020	av 15,851

A value of M_c was also calculated from the tensile modulus E derived from stress-strain data measured at 80° C with the Instron tensile tester. The modulus was evaluated, as described elsewhere[7], from the slope of a plot of αS vs. γ, where αS is the stress based on the stressed cross-sectional area of a specimen and γ is the strain. At 80° C, the modulus was found to decrease from 7.35 to 6.58×10^6 dynes/cm^2 as the strain rate of the test was decreased from 1.516×10^{-2} to 1.516×10^{-4} sec^{-1}. At 60° C and a strain rate of 1.516×10^{-3}, the modulus was 6.96×10^6 dynes/cm^2. These data indicate that the value measured at the lowest rate at 80° C is a near-equilibrium one. By substituting $E = 6.58 \times 10^6$ at $T = 353°$ K in the equation $M_c = 3\rho RT/E$, it is found that $M_c = 13{,}100$, in fair agreement with 15,800 obtained from swelling data (Table I).

Unfortunately, M_c values for the vulcanizate studied previously were 8020 and 9250 as obtained from swelling and modulus data, respectively. The difference in M_c of the two vulcanizates precludes quantitative comparisons of the ultimate properties of the first vulcanizate, studied at constant strain rates, with those observed on the present vulcanizate under constant strain conditions. Because of the desire to compare results obtained under these

different conditions, some measurements under constant strain rates were also made on the present vulcanizate.

APPARATUS

Data under both constant strain rate and constant strain conditions were measured on rings which were cut from the sheets of SBR with a circular die which had an inside diameter of 1.400 in. and an outside diameter of 1.650 in. The edges of the die-cut rings were dished slightly, although this slight imperfection was disregarded in measuring the dimensions of specimens. Tensile data were measured at different temperatures, and strain rates with an Instron tensile tester equipped as briefly described previously[1].

The constant strain apparatus[7] contained eight racks for stretching ring specimens. These racks were mounted in an air thermostat whose temperature was controlled by the continuous circulation of heated or refrigerated air from an external source. Temperature control devices maintained the temperature at any given point to within $\pm 0.5°$ C for many hours; the maximum temperature difference between various points in the thermostat was about 1° C. When the temperature was regulated below ambient for several days or more, the over-all temperature variation, as indicated by three thermocouples, was about $\pm 1.5°$ C, this large variation being due to certain operational changes produced by frosting of the refrigeration coils. During operation, a stream of dry nitrogen was bled continuously into the system to delay frosting.

Each rack for stretching a specimen consisted of a vertically mounted brass rod on which two movable supports were attached. Each support had a freely rotating nylon pulley whose diameter was 0.150 in., and a ring type specimen was placed over the pulleys. The upper support was connected to a heat treated steel beam which rested on knife edges mounted on top of the thermostat, and the lower support was connected by a cable to a wheel mounted under the thermostat. By adjusting the position of a metal stop on the brass rod, the specimen could be stretched manually by the wheel and cable device to a predetermined elongation in 2 sec. or less. The force exerted by a stretched specimen was determined by measuring the small deflection of the beam with a linear variable differential transformer whose output was recorded by a Brown potentiometer; the output was determined to be a linear function of the applied force within about 1%.

Ultimate properties under constant strain conditions were measured on eight samples simultaneously. To carry out tests, unstrained rings of SBR were placed over the pulleys on the racks and allowed to come to temperature equilibrium. The rings were then rapidly stretched to predetermined elongations, the elongation increment of adjacent specimens normally being 25%. The elongations were calculated from the final distance between the centers of the pulleys, the diameter of the pulleys, and the initial inside diameter of a ring. The inside diameter was used to obtain the maximum elongation existing in a stretched ring. Other experimental work has indicated that the maximum elongation, instead of some average value, correlates best with the ultimate elongation measured on tensile specimens in which the strain is uniform. To obtain the stress, the measured load on the supporting beam was divided by twice the initial cross-sectional area of the ring. Because of some uncertainties in determining the absolute value of the load during a measurement and in determining the cross-sectional area of a specimen, the error in the stress may at times have been as great as 10%.

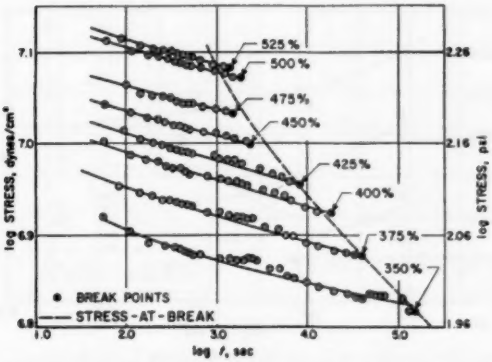

FIG. 3.—Stress-relaxation of an SBR rubber at 1.7° C under elongations from 350 to 525%. Solid points indicate rupture.

III. RESULTS AND DISCUSSION

Stress-relaxation measurements were made at various elongations at eight temperatures between 1.7° and 60° C, most measurements being continued until rupture occurred. (A few measurements were also made at −5° and −15° C, but the rupture data were erratic and thus are not presented.) Stress-relaxation data obtained during a typical run are shown in Figure 3. These data were measured at 1.7° C and at eight elongations between 350 and 525%. The solid points indicate when rupture occurred and the dotted curve through these points shows the stress at break at the various elongations.

Plots are shown in Figure 4 of the percent elongation against the logarithm of the time to break (t_b) for results obtained at 1.7°, 7.2°, 12.8°, and 18.3° C; data obtained at 29.4°, 40°, and 50° C are shown in Figure 5. Two sets of measurements were made at each temperature and the results from each are differentiated by flags on the points. Figures 6 and 7 show plots of log S_b $286/T$ vs. log t_b, where S_b is the stress at break and T is the absolute temperature of measurement. As shown in Figure 6, only one set of stress measurements

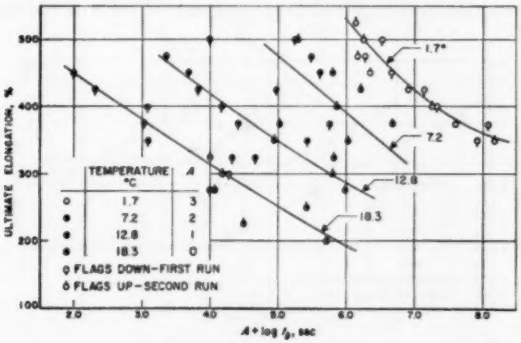

FIG. 4.—Variation of ultimate elongation with log t_b under constant elongations (values of A are arbitrary).

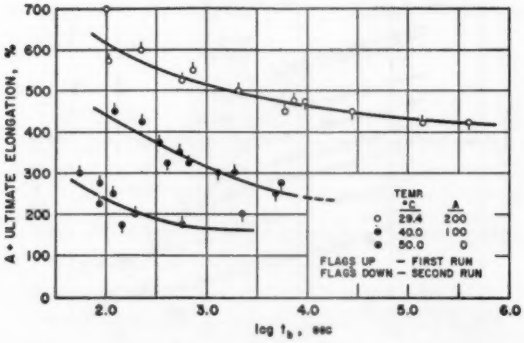

FIG. 5.—Variation of ultimate elongation with log t_b under constant elongations (values of A are arbitrary).

was made at 1.7° C, although as shown in Figure 4, two sets of time-to-break measurements were made at this temperature. (For clarity, the data in Figures 4 and 6 are shifted along the abscissa by arbitrary amounts A and, similarly, along the ordinate in Figures 5 and 7.) Because elastic retractive forces are directly proportional to the absolute temperature, all values of the stress at break are multiplied by $286/T$ to reduce them to 286° K. (The ultimate property data obtained at 60° C under the constant strain conditions are shown later by the points in Figures 10 and 11.) Because values of the ultimate properties are by nature rather nonreproducible, the scatter of the points about the lines shown in the figures is not unduly great, except for the data at 7.2° C.

Both the ultimate elongation and stress-at-break data at the various temperatures were superposed by shifting along the log t_b axis to obtain values of the shift factor a_T. The shape of some curves representing data at the higher temperatures changes markedly with temperature, and the shift distance required to superpose these curves was selected somewhat arbitrarily. For the 29.4° and 40° C data, the best over-all superposition—which actually is rather poor—is effected by an unusually large shift. Because this large shift was inconsistent with that required to give superposition of other data separated

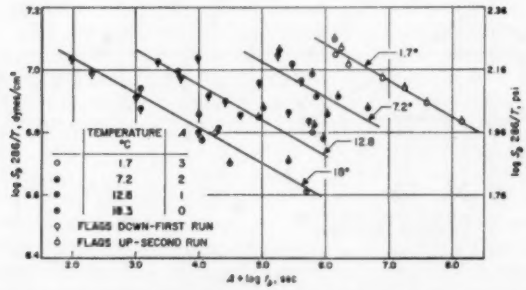

FIG. 6.—Logarithm of the stress at break reduced to 286° K (S_b 286/T) plotted against log t_b. Data obtained under constant elongations (values of A are arbitrary).

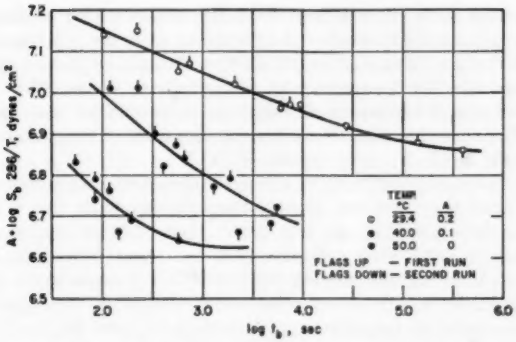

FIG. 7.—Log S_b 286/T plotted against log t_b. Data obtained under constant elongations (values of A are arbitrary).

by 10° C, superposition was effected by considering only the first three or four points at the low end of the time scale at 40° C. This procedure gave a reasonably realistic value of the shift factor. In general, however, the accuracy of the a_T values is markedly lower than of those presented previously[1], obtained by superposing ultimate property data measured at different strain rates. However, values obtained for log a_T are compared in Figure 8 with the WLF equation. The solid square point in Figure 8 shows that 12.8° C was selected as the reference temperature for the experimental determination of a_T values by shifting data.

Figure 8 shows that at 29.4° C and higher temperatures the values of log a_T obtained from the stress-at-break data are not in close agreement with those

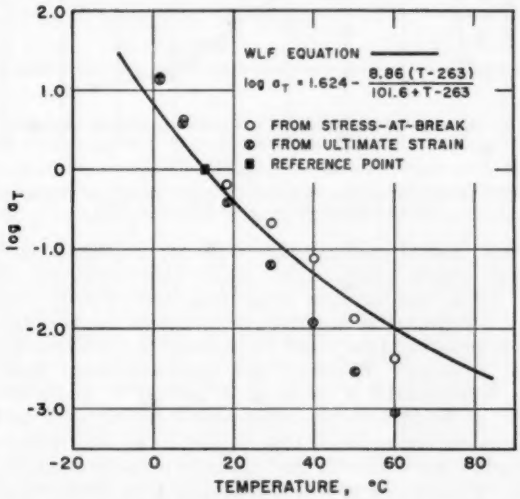

FIG. 8.—Shift factor log a_T obtained by superposing ultimate property data compared with the WLF equation.

from the ultimate elongation data. Actually, values of log a_T from the stress-at-break data seem to be in moderate agreement with the WLF equation except at 50° and 60° C, whereas values from the elongation data begin to depart markedly from the WLF equation at temperatures above 29.4° C. A small deviation from the WLF equation might be expected at temperatures above about 40° C because this equation often applies only at temperatures less than $T_s + 50$; for the SBR, $T_s + 50$ equals 40° C.

Because of the poor accuracy of the a_T values, the only conclusion that can be drawn is that they are not grossly inconsistent with the WLF equation. However, the data certainly do not prove that rupture under conditions of constant strain is controlled entirely by the internal viscosity, as would be shown if the values agreed closely with the WLF equation. Actually, the stress-relaxation data, discussed elsewhere[7], suggest that some chemical degradation occurred during the experiments at 50° and 60° C. Although the

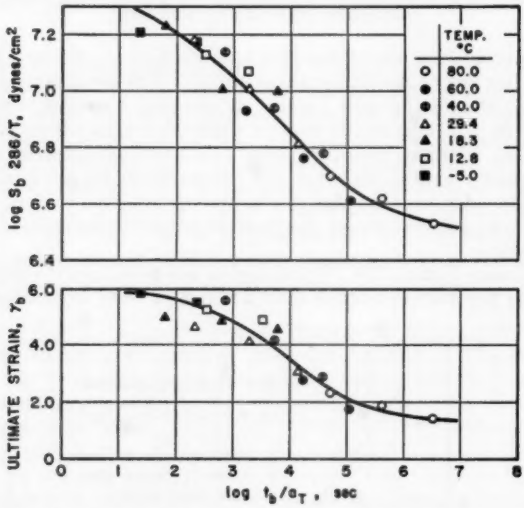

FIG. 9.—Ultimate properties measured at different strain rates and temperature plotted against log t_b. Data reduced to 13° C.

thermostat was flushed continuously with dry nitrogen, as mentioned in Section II, the oxygen concentration in the thermostat was only one-third that in air. Thus, the nitrogen purge was ineffective to prevent possible degradation. If degradation occurred, the values of log a_T obtained by superposing ultimate property data would be expected to differ from those predicted by the WLF equation. However, the stress-relaxation data showed degradation only after about 6×10^4 sec at 50° and 60° C; under these conditions, only two values of the ultimate properties were obtained (see Figures 10 and 11). Thus, there is no definite evidence that rupture times were influenced by degradation, although it is conceivable that ultimate property data are affected to a greater extent by small amounts of degradation than stress-relaxation data.

Because of the difficulty in choosing a reliable set of log a_T values, the ultimate properties at the various temperatures are not shown plotted against

the time to break reduced to a common temperature. Although such reduced plots can be constructed, their reliability for predicting values of the ultimate properties over an extended time scale at different temperatures would be questionable. Values of the ultimate properties observed under constant strain conditions at a given temperature will thus be compared directly with the values measured at different strain rates.

The ultimate properties at different strain rates were measured at seven temperatures between $-5°$ and 80° C and at three strain rates at most of these temperatures. The strain rates ranged from 1.52×10^{-4} to 1.52×10^{-1} sec^{-1}, although this range was not covered at any single temperature. The few data obtained at each temperature coupled with the poor reliability of individual values of the ultimate properties precluded the determination of accurate values of log a_T by shift plots of the data at each temperature to effect superposition. Because the previous study[1] showed that values of a_T given by the WLF equation can be used to effect superposition, the present data were superposed by using the a_T values shown by the plot of the WLF equation in Figure 8. The resulting curves are shown in Figure 9, where the ultimate strain and log S_b $286/T$ are plotted against log t_b/a_T, the quantity t_b/a_T being the time to break reduced to 286° K.

To compare the data measured at constant strain rates with those at constant strains, the curves in Figure 9 were reduced to each of the temperatures at which constant strain measurements were made; this reduction was made by using values of log a_T given by the WLF equation in Figure 8 to change the time scale. Sections of the curves reduced to 29.4°, 40°, 50°, and 60° C are compared in Figures 10 and 11 with the constant strain data measured at these temperatures. In the figures, sections of the reduced curves are shown by solid lines and the individual values measured at constant strain rates at 29.4°, 40°, and 60° C (measurements were not made at 50°) are shown by points; the dotted lines show the constant strain data, and individual values obtained under these conditions are shown at 60° C. Plots like those in Figures 10 and 11 were also prepared from data at 1.7°, 7.2°, 12.8°, and 18.3° C. Because these plots did not show any trends not shown by Figures 10 and 11, they are not presented.

Figures 10 and 11 show that most individual values obtained at constant strain rates lie to the right of the curves showing values measured at constant strain. Although the curves showing the constant strain rate data lie to the right of those showing constant strain data—at least at shorter times—the curves at 29.4° C intersect so that at long times the constant strain rate data lie to the left of the constant strain data. This crossover is unexpected and probably is not real, especially since no individual values measured at constant strain rate lie below or to the left of the curves showing the constant strain data.

A crossover of the curves indicates that at long times the time to break for a sample under constant strain is greater than for a sample subjected to a constant strain rate. However, under constant strain conditions, the energy input to a sample as measured by the product of stress and elongation is considerably greater than the energy input to a sample which is strained continuously at a constant rate until rupture occurs. This factor suggests that the time to break for samples under constant strain should not be longer than for samples subjected to a constant strain rate. Thus, the crossover is tentatively attributed to some error in either the experimental data or its reduction.

An attempt was made to measure ultimate properties under constant

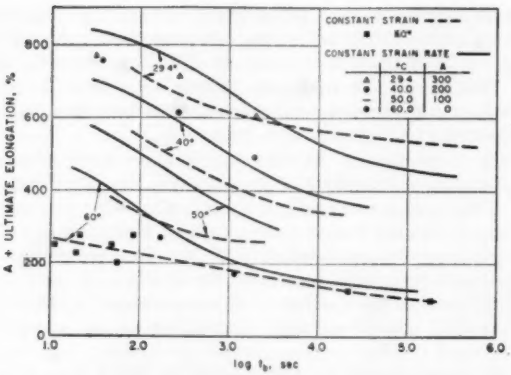

FIG. 10.—Comparison of ultimate elongation vs. log t_b data measured at constant elongations with values measured at different strain rates (values of A are arbitrary).

elongations at −5° and −15° C. The results were erratic and thus are not presented. At these low temperatures, it is possible that during the stretching of a specimen to certain elongations, the left side of the bell-shaped curve—like that shown in Figure 1—was often approached rather closely. If this were true, the time of stretching a specimen could affect the results because a small difference in time would change markedly the closeness of approach to the bell-shaped curve. Thus, in some tests, damage may have been done to the network when a specimen was stretched; this damage could cause the specimen to break almost immediately or to break at times considerably different than expected; both types of behavior were observed. When the bell-shaped curve is not closely approached during the stretching of a specimen, no damage should be done to the specimen. However, the time to break might now be greater than the four to five days normally used for a test and no rupture of the specimen would be observed.

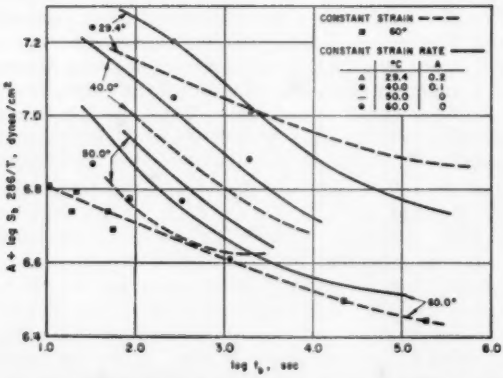

FIG. 11.—Comparison of log S_b 286/T vs. log t_b data measured at constant elongations with values measured at different strain rates (values of A are arbitrary).

SYNOPSIS

The ultimate properties of amorphous rubbers at temperatures above T_g are considered in terms of stress-strain curves to rupture measured at different strain rates and temperatures. The consideration indicates that a specimen held at a fixed elongation should break eventually, provided the elongation exceeds a critical value. This expected behavior was found by studying an SBR rubber. For samples maintained at different elongations for up to seven days, both the time to break and the stress at break were measured at eight temperatures from 1.7° to 60° C. For comparison, the ultimate properties were also measured at different strain rates and temperatures. The comparison indicates that for a given ultimate elongation and stress at break, the time to break under conditions of constant elongation is less than under conditions of constant strain rate.

ACKNOWLEDGMENTS

The authors wish to acknowledge the contributions of C. W. Weekly, who assisted in the performance of the experiments, and the cooperation of the Computer and Design Groups of the Jet Propulsion Laboratory.

REFERENCES

[1] Smith, T. L., *J. Polymer Science* **32**, 99 (1958).
[2] Williams, M. L., Landel, R. F. and Ferry, J. D., *J. Am. Chem. Soc.* **77**, 3701 (1955).
[3] Bueche, F., *J. Appl. Phys.* **26**, 1133 (1955).
[4] See for example, R. N. Haward, "Strength of Plastics and Glasses", Interscience Publishers, Inc., New York, 1949 and F. Schwarzl and A. J. Stoverman, "Die Physik der Hochpolymeren", ed. H. A. Stuart, Springer Verlag, Berlin, Germany, 1956, Vol. IV, Chapter III.
[5] Howard, R. N., *Trans. Faraday Soc.* **39**, 267 (1943).
[6] Landel, R. F. and Stedry, P. J., preceding paper, this issue.
[7] Smith, J. L. and Magnusson, A. B., *J. Polymer Sci.* **42**, 391 (1960).

OXIDATIVE STRESS RELAXATION STUDIES OF RADIATION CURED VULCANIZATES, WITH AND WITHOUT ANTIOXIDANT *

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INTRODUCTION

Turner has shown that irradiation of natural rubber results in the formation of carbon to carbon crosslinks by combination of allylic radicals[1]; the same type of crosslinks are formed by heating rubber in presence of organic peroxides[2]. Since peroxide vulcanizates may be freed from excess vulcanizing ingredients and by products by extraction while radiation crosslinking may be effected without additive, it is expected that the two types of vulcanizate should age in an analogous manner. The present study was undertaken in order to see whether radiation vulcanizates did show the same aging behavior as peroxide vulcanizates according to measurements of oxidative stress relaxation[3], and, if so, to ascertain whether the efficiency of antioxidants of the dithiocarbamate type was affected by the irradiation and whether such materials had an adverse effect upon cure.

It has been stated that radiation vulcanizates are resistant to aging even in the absence of antioxidant and their stability has been attributed to the presence of purely carbon-carbon crosslinks[4]. However, it has recently been demonstrated that a carbon-carbon crosslink is not a sufficient condition for vulcanizate stability in the absence of antioxidant[3]. Previous studies concerning the aging of radiation cures appear to have been made using materials containing carbon black, which is now known to act as an antioxidant[5]; it is necessary, for work of fundamental significance, to use gum stocks based on very pure rubber.

EXPERIMENTAL

Methods.—Aging has been followed by measurements of both continuous and intermittent stress relaxation at various temperatures and also in ultraviolet light. The technique and apparatus have been fully described elsewhere (e.g. refs. 3 and 6); stress relaxation data (Figures 1–6) are plotted as the logarithm of (stress (f) at time t divided by initial stress f_0) against time. In all cases the samples were extended only 50% to minimize the risk of the sample tearing during aging. Some confirmatory experiments regarding the lifetime of antioxidants have been made in an automatically operated constant pressure oxygen uptake apparatus which also is described elsewhere[7].

Materials.—Vulcanizates were prepared by irradiating 0.02 cm thick films of natural rubber cast from a 2% solution in benzene in aluminium foil boats floating on mercury. The boats were warmed with infrared lamps and a

* Presented before the Deutsche Kautschuk-Gesellschaft, Vortragstagung 4.–8. October 1960 in West Berlin; *Kautschuk und Gummi* 14, WT114 (1961).

stream of nitrogen passed over them to prevent oxidative degradation and assist the removal of benzene vapor which was condensed in a trap cooled in an acetone-Dry Ice bath. The rubber employed was either acetone extracted deproteinized (DP) crepe (supplied by the Indonesian Rubber Research Organization) or extracted "Highly Purified" (HP) rubber (U. S. Rubber Co.) both of which had a low nitrogen content[3a]. These rubbers were lightly milled so as to facilitate solution in benzene.

The principal source of radiation employed was the electron beam from a 4 MeV linear accelerator at Wantage Radiation Laboratory. Samples to be crosslinked by this means, retained on a backing of aluminum foil, were sealed in glass tubes at less than 10^{-4} mm pressure and water cooled during irradiation. The radiation dose given was varied according to the degree of crosslinking required and degrees of crosslinking, expressed as the elastic network parameter C_1 obtained from measurements of equilibrium swelling[8] in *n*-decane at 25° C, together with the dosages in Mrads, are tabulated at the appropriate points in the text.

Some samples were irradiated in the atomic pile at A.E.R.E. Harwell (B.E.P.O.), in which case they were packed in aluminum cans which were flushed with nitrogen and sealed with latex. Such treatment did not ensure such complete absence of oxygen as did sealing in vacuum. Pile irradiated samples containing dithiocarbamate were stored for some weeks at Harwell until induced radioactivity had decayed to a safe value.

Zinc di-*iso*propyl- and di-*sec*-butyldithiophosphates were prepared as described elsewhere[9], zinc morpholino-1-carbodithioate was kindly donated by Dr. B. Saville and the other additives used were good quality commercial materials recrystallized when necessary. Introduction of additives after crosslinking was effected by swelling the vulcanizates in ethyl acetate solutions of the required materials.

RESULTS

The continuous and intermittent stress relaxation of an unprotected 40 Mrad electron beam vulcanizate of DP crepe (C_1 = 1.13) is autocatalytic at

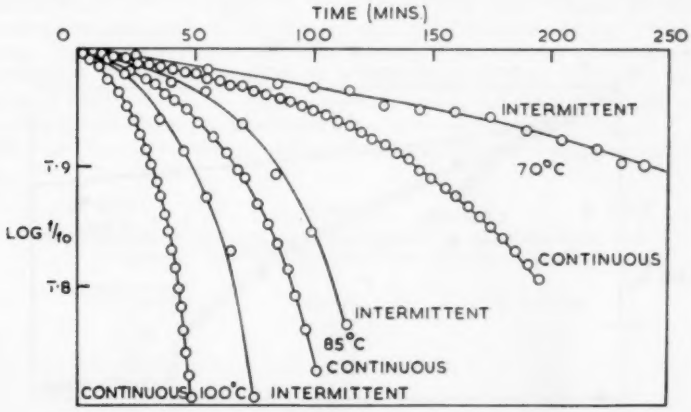

FIG. 1.—Continuous and intermittent relaxation of radiation vulcanizates in air at 70°, 85° and 100° C.

TABLE 1

THE STRESS RELAXATION OF A RADIATION VULCANIZATE OF EXTRACTED DEPROTEINIZED CREPE IN AIR AT 100° C IN PRESENCE OF ADDITIVES INTRODUCED BY SWELLING

Additive	Time (mins)	f/f_0			
		ZnDBDC	BBC	ZnID	2246
	200	0.9570	0.9519	0.9506	0.9614
	515	0.8760	0.8969	0.8718	0.8606
	1950	0.8570	0.8768	0.8502	0.8117
	4110	0.8224	Ruptured	0.7881	0.6471
	4530	0.8151		0.7720	0.6320
	5470	0.7991		0.7409	0.5302

70°, 85° and 100° C. (Figure 1); the intermittent relaxation is slower than the continuous in each case, particularly at 70° C, indicating that some crosslinking occurs during aging.

The initial rate of relaxation of a radiation vulcanizate (50 Mrad cure; $C_1 = 1.570$) at 100° C in air in presence of zinc dibutyldithiocarbamate (ZnDBDC) or Antioxidant 2246, swollen in from saturated solution or of dibutylammonium dibutyldithiocarbamate (BBC) or zinc di-*iso*propyldithiophosphate (ZnID) swollen in from 1% solution in ethyl acetate was very slow (Table 1). The marked response to the presence of antioxidants, and particularly of dithiocarbamates and related materials as well as the absence of degradation in vacuo (Figure 4) is analogous to the behavior of extracted peroxide vulcanizates[3].

At 70° C the relaxation in oxygen of a sample freshly taken from its evacuated glass tube was initially very slow (Figure 2) and the introduction of Antioxidant 2246 from 0.2% ethyl acetate solution did not affect this initial rate, although it prolonged the period of slow relaxation. Introduction of ZnDBDC from 0.2% solution resulted in a reduced rate of relaxation, except in the very early stages and in a considerable increase in the period of slow relaxation.

Some data have been obtained on the stress relaxation of vulcanizates of extracted deproteinized crepe crosslinked in the atomic pile in presence and absence of 1% ZnDBDC (Figure 3). The ZnDBDC powerfully inhibits the

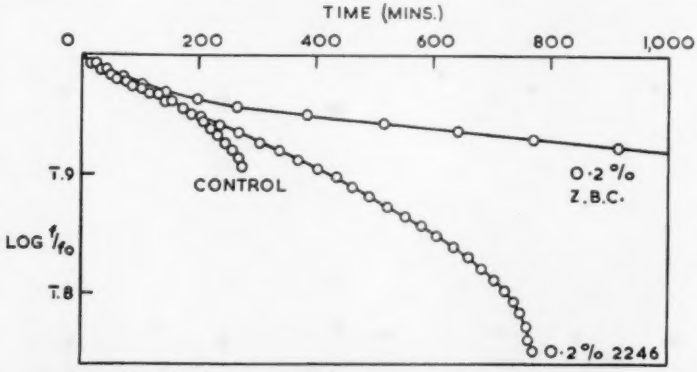

FIG. 2.—Stress relaxation at 70° C in oxygen of a radiation vulcanizate containing 0.2% 2246 or ZnDBDC introduced by swelling.

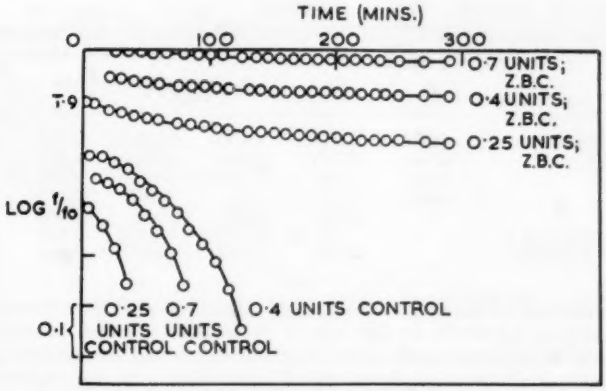

FIG. 3.—Stress relaxation in air at 100° C of pile radiation cures with and without zinc dibutyl-dithiocarbamate.

oxidative degradation in air at 100° C of vulcanizates of various degrees of crosslinking, but it reduces the number of crosslinks introduced by a given dose of radiation (Table 2).

The effect of 1% of various additives on the degree of crosslinking for a given dose has been more fully investigated by examining a series of samples crosslinked in the electron beam using dosages from 20 to 100 MRad (Table 3). In presence of zinc di-*iso*propyldithiophosphate the degree of crosslinking for a given radiation dose is not reduced. Both zinc and dibutylammonium dibutyldithiocarbamates reduce the degree of crosslinking for a given dose by about one third and Antioxidant 2246, with or without other additive, reduces it by about one half.

Stress relaxation data have been obtained at 100° C in air for radiation vulcanizates crosslinked to the same degree ($C_1 \simeq 1.0$) in presence of the additives listed above (Figure 4). ZnDBDC and ZnID reduce the initial relaxation rate practically to the *in vacuo* rate, but BBC scarcely protects at all, although if introduced into a control by swelling it has initially a very powerful effect (Table 1). Antioxidant 2246 is less effective than ZnDBDC and a mixture of 0.5% of each of these materials confers on the vulcanizate aging properties intermediate between those found with each antioxidant alone. The presence of Tinuvin P does not influence thermal aging of a sample containing 2246.

TABLE 2

DEPENDENCE OF DEGREE OF CROSSLINKING OF RUBBER WITH AND WITHOUT ZnDBDC ON THE PILE RADIATION DOSE

Radiation dose (Pile Units)*	Control	C_1 2% ZnDBDC
0.25	0.826	0.587
0.4	0.996	0.626
0.5	1.546	1.019
0.7	2.188	1.382
1.0	2.95	2.037

* One pile unit is the radiation associated with an integral thermal neutron flux of 10^{17}/sq cm.

TABLE 3

THE INFLUENCE OF 1% OF DIFFERENT ADDITIVES ON THE DEGREE OF CROSSLINKING OF RUBBER BY DIFFERENT RADIATION DOSES

Radiation dose (Mrad) Additive	20	40	50	60	80	100
	C_1 values					
None (control)	0.671	1.213	1.570	1.680	2.162	2.490
ZnDBDC	0.344	0.708	0.855	0.940	1.205	1.886
BBC	0.367	0.595	0.790	1.002	1.380	2.118
ZnID	0.695	1.171	—	1.815	2.118	2.515
2246	—	0.642	0.720	—	1.080	
2246 + Tinuvin P		0.720	0.703	0.810	0.827	
2246 + ZnDBDC		0.520	0.725	0.984	0.856	

The influence of molecular weight and solubility of dithiocarbamate and dithiophosphate additives on the degree of crosslinking and on antioxidant lifetime has been investigated using vulcanizates based on extracted highly purified rubber all crosslinked with 40 Mrad radiation in the electron beam (Table 4). Unlike zinc dibutyldithiocarbamate, zinc dimethyldithiocarbamate (ZnDMDC) and zinc morpholino-1-carbodithioate do not affect the degree of crosslinking. Zinc di-*iso*propyldithiophosphate renders crosslinking somewhat more efficient, whereas the corresponding di-*sec*-butyl-compound reduces it slightly.

Considering aging in oxygen at 100° C (Figure 5), stress relaxation in presence of ZnDMDC proceeds at a slow rate for far longer (16 days) than in presence of any other additive studied, and in that time 40% of the original network is destroyed. ZnDBDC protects relaxation for only 4500 minutes, and oxygen uptake in presence of ZnDBDC is rapid after 7000 minutes. ZnID is practically as long lived as ZnDBDC, but zinc di-*sec*-butyldithiophosphate gives no appreciable protection.

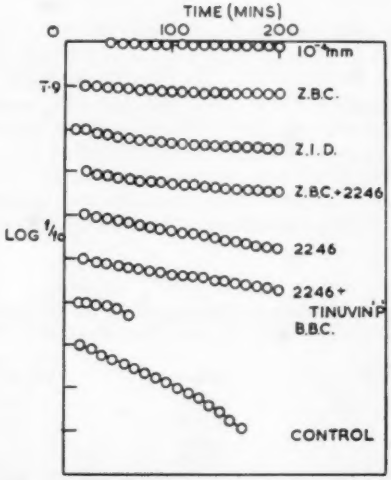

FIG. 4.—Stress relaxation at 100° C in air of electron beam radiation vulcanizates crosslinked to C ≃ 1.0 in presence of additives.

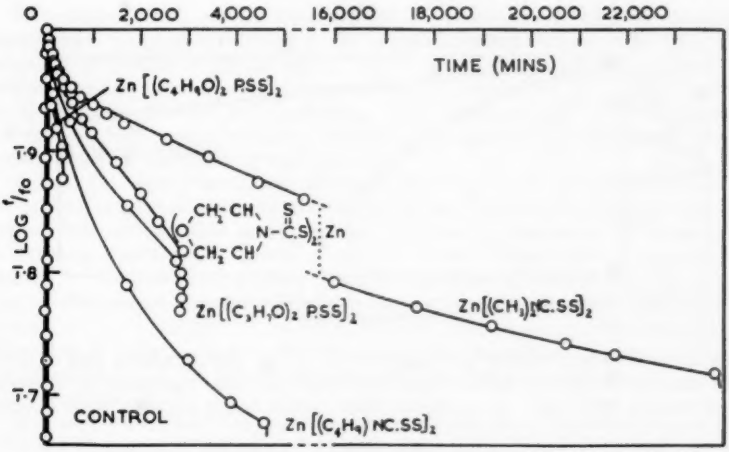

FIG. 5.—Stress relaxation at 100° C in oxygen of radiation vulcanizates crosslinked in presence of sulfur containing antioxidants.

The photochemical aging in light of wavelength 313 mμ and above of samples irradiated in presence of 1% 2246 with and without 1% Tinuvin P has been examined (Figure 6). The aging is much improved in presence of the UV absorber Tinuvin P.

DISCUSSION

As might be expected from the similarity of their network structures uninhibited radiation vulcanizates exhibit aging behavior similar to that of peroxide vulcanizates[3]. Thus the degradation is autocatalytic (Figure 1) and ceases in the absence of oxygen. Efficient antioxidants have a very marked effect upon the rate of the degradation which, in their presence, is no longer autocatalytic, and dithiocarbamates or related compounds are particularly beneficial (Table 1; Figure 4). In the case of peroxide vulcanizates such behavior was taken to indicate that scission occurred as an alternative to the initiation or propagation step of an autoxidation whose mechanism was analogous to that proposed for olefinic hydrocarbons in presence of retarder and the experimental results obeyed the force-time relationship

$$\frac{f}{f_0 - f} = \frac{a}{t} - b$$

which is based on such a mechanism.

When plotted as $f/(f_0 - f)$ against $1/t$ the data for stress relaxation of radiation vulcanizates obtained in air at 85° and 100° C (Figure 1) yield excellent linear plots (Figure 7) confirming the similarity in aging of radiation and peroxide vulcanizates. The data obtained at 70° C do not give a linear plot of $f/(f_0 - f)$ against $1/t$ and the curves of log f/f_0 against $1/t$ in this instance are initially linear and not autoaccelerative. Since 0.2% of 2246 does not lower the initial rate of relaxation at 70° C (Figure 2) it appears that the vulcanizate contains traces of an efficient antioxidant which appreciably lowers the autoxidation chain length in the early stages of degradation[10]. The effect of

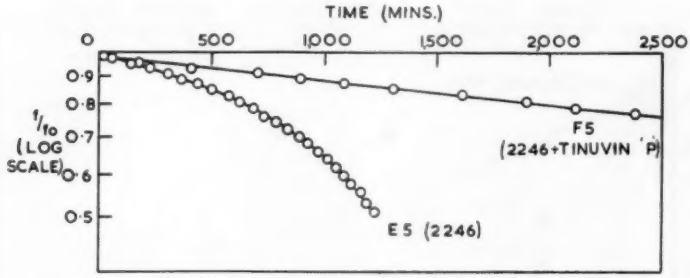

FIG. 6.—Stress relaxation in 313 m/μ light of radiation vulcanizates containing 2246 with and without Tinuvin P.

such an antioxidant would be longest lived at low temperatures and at such low concentrations of rubber hydroperoxide as those present in samples irradiated at 10^{-4} mm. It is known that carbon black together with natural

TABLE 4

THE DEGREE OF CROSSLINKING OF EXTRACTED HP RUBBER, GIVEN 40 MRAD RADIATION IN PRESENCE OF VARIOUS ADDITIVES

Additive	C_1
None	1.28
Zinc dibutyldithiocarbamate	0.83
Zinc dimethyldithiocarbamate	1.32
Zinc morpholino-1-carbodithioate	1.33
Zinc di-*iso*propyldithiophosphate	1.75
Zinc di-*sec*-butyldithiophosphate	1.10

antioxidants adequately protects rubber vulcanized by radiation *in vacuo*, whereas the same mix vulcanized in air ages rapidly[11], on account of its high initial content of rubber hydroperoxide.

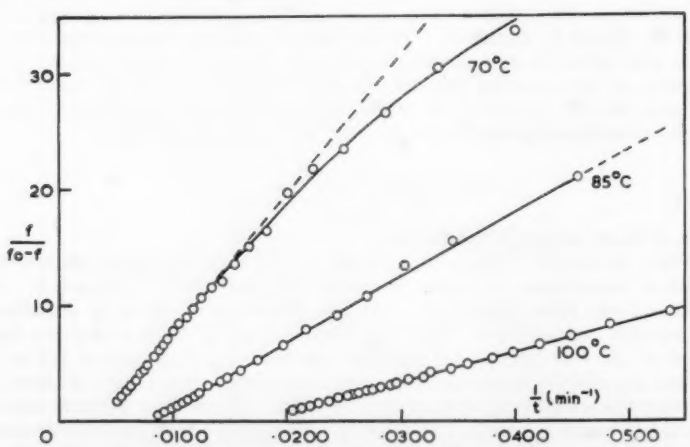

FIG. 7.—Theoretical interpretation of data from Fig. 1.

The intermittent relaxation of radiation vulcanizates, and of peroxide vulcanizates also, is slower than the continuous relaxation indicating the formation of crosslinks during aging. In radiation vulcanizates the difference between the two types of stress relaxation is most marked at 70° C and, according to Tobolsky, there is no crosslinking during aging at 130° C[12]. The crosslinking may be brought about by vinylidene groups in the vulcanizate whose concentration is increased by radiation[1].

Certain dithiocarbamates and dithiophosphates reduce the initial relaxation rate and extend the lifetime of radiation vulcanizates more than do conventional antioxidants such as 2246, whether introduced before irradiation or introduced by swelling afterwards. The efficiency of some of these thio compounds is affected by the irradiation; thus dibutylammonium dibutyl dithiocarbamate does not protect if introduced before irradiation and zinc dibutyldithiocarbamate, which is comparable in efficiency and lifetime to zinc dimethyldithiocarbamate if introduced into radiation or peroxide vulcanizates by swelling, is much inferior to the dimethyl analogue if introduced into the mix before radiation vulcanization.

It is well known that conventional antioxidants and other radical acceptors lower the degree of crosslinking for a given radiation dose[13, 14]; 2246, for instance, reduces the degree of crosslinking by half. Those dithio compounds, such as zinc or dibutylammonium dibutyldithiocarbamates or zinc di-*tert*-butyldithiophosphate, which are less efficient if introduced before irradiation than if introduced into a radiation vulcanizate by swelling, also markedly reduced the degree of crosslinking. On the other hand, zinc dimethyldithiocarbamate, which retains its efficiency after irradiation, and zinc di-*iso*propyldithiophosphate do not inhibit radiation crosslinking. In fact zinc di-*iso*propyldithiophosphate appears to aid network formation. The dithio-compounds of lower molecular weight, which are less soluble in rubber, are both the least damaging to the cure and the most efficient antioxidants. Turner has suggested that these are not sufficiently soluble to maintain an appreciable concentration of radical acceptor during the fast reaction resulting from the irradiation, whereas they may be soluble enough to maintain a constant inhibitor concentration in a slowly oxidizing system. Those inhibitors which do inhibit crosslinking are destroyed in the process and their subsequent lifetime as antioxidants is reduced. Zinc morpholino-1-carbodithioate represents the extreme case, being insufficiently soluble even to protect adequately against oxidative degradation.

The present investigation shows that zinc dimethyldithiocarbamate is far more effective in protecting radiation vulcanizates against oxidative aging at 100° C than are any of the other materials studied (Figure 6), but there may be other thio compounds which have similar efficiency.

Tinuvin P retains its ability to absorb UV light when introduced into a radiation vulcanizate before cure, and thus it should be possible to produce light stable radiation vulcanizates[15].

ACKNOWLEDGMENTS

The author wishes to thank Dr. R. Roberts and Mr. J. McCann for making available the irradiation facilities at the Wantage Radiation Laboratory, and Dr. D. Turner for communicating the samples to Wantage and also for helpful suggestions concerning the work. He is grateful to Mr. R. Tiller for his help in carrying out the experiments. This work forms part of the research program of The Natural Rubber Producers' Research Association.

SUMMARY

The oxidative aging of purified rubber crosslinked by γ-radiation both in the atomic pile and in the electron beam has been studied by measurements of continuous and intermittent relaxation. Degradation at 70–100° C in air has been shown to proceed through autocatalytic scission of the polyisoprene chains which is markedly retarded by phenolic antioxidants and particularly by dithiocarbamates. The data obtained at 85° and 100° C. accurately obey the force-time relationship

$$\frac{f}{f_0 - f} = \frac{a}{t} - b$$

which is predicted for degradation during an autoxidation chain similar to that occurring in olefins. This behavior was exhibited by peroxide vulcanizates which also contain carbon-carbon crosslinks.

Conventional antioxidants and rubber soluble dithiocarbamates or dithiophosphates inhibit the crosslinking reaction and give rise to a softer product for a given radiation dose. By virtue of their acting as inhibitors of crosslinking the concentration of these materials is reduced during radiation curing and their subsequent lifetime as antioxidants is therefore reduced. The less soluble dithiocompounds of lower molecular weight do not inhibit the crosslinking reaction, and their concentration after cure is unchanged. Certain of these are sufficiently soluble to inhibit autoxidation, and their efficiency in that capacity is unchanged. The most efficient antioxidant for introduction at a concentration of 1% into mixes for radiation vulcanization is zinc dimethyl dithiocarbamate. This does not affect the cure, and it protects the vulcanizate against oxidative degradation at 100° C for considerably longer than any of the other materials investigated, including zinc dibutyldithiocarbamate which would be comparably efficient if introduced from solution after cure.

Experiments involving introduction of Tinuvin P before cure show that transparent radiation vulcanizates may be protected from photochemical degradation by the addition of UV absorbers.

REFERENCES

[1] Turner, D. T., *Polymer* **1**, 27 (1960); following paper, this issue.
[2] Moore, C. G. and Watson, W. F., *J. Polymer Sci.* **19**, 237 (1956).
[3] (a) Dunn, J. R., Scanlan, J. and Watson, W. F., *Trans. Faraday Soc.* **55**, 667 (1959).
(b) Dunn, J. R., *Rev. gén. caoutchouc* **36**, 1869 (1959).
[4] Stockman, C. H., Harmon, D. J. and Neff, H. F., *Nucleonics*, **15**, 94 (1957).
[5] Bevilacqua, E. M., *J. Am. Chem. Soc.* **81**, 5071 (1959).
[6] Dunn, J. R. and Scanlan, J., *J. Appl. Polymer Sci.* **4**, 34 (1960).
[7] Scanlan, J. and Dunn, J. R., *J. Scientific Instr.* **38**, 24 (1961).
[8] Mullins, L., *J. Polymer Sci.* **19**, 225 (1956).
[9] Dunn, J. R. and Scanlan, J., *J. Polymer Sci.* **35**, 267 (1959).
[10] Ore, S., "On the Oxidative Stress Relaxation of Natural Rubber Vulcanized with Di-*tert* butyl Peroxide" (Oslo University Press 1958).
[11] Ossefort, Z. T., *Rubber World* **140**, 69 (1959).
[12] Tobolsky, A. V. and Mercurio, A., *J. Appl. Polymer Sci.* **2**, 186 (1960).
[13] Pinner, S. H., *Int. J. of Applied Rad. & Isotopes* **5**, 121 (1959).
[14] Turner, D. T., *J. Polymer Sci.* **27**, 503 (1958).
[15] Dunn, J. R. and Fogg, S. G., *J. Appl. Polymer Sci.* **2**, 367 (1959).

THE PROTECTION OF TRANSPARENT VULCANIZATES AGAINST AGING IN SUNLIGHT *

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Care has to be taken in choosing antioxidants for use in transparent natural rubber vulcanizates since some amines commonly employed as protective agents against thermal degradation photosensitize aging in ultraviolet (uv) light[1]. Further studies[2] using the technique of stress relaxation, undertaken in order to find the most satisfactory type of antioxidant for protection against sunlight aging, have shown that, with additives introduced into extracted samples of peroxide vulcanizate by swelling from ethyl acetate solution, the best results were obtained using a mixture of a substituted bis-phenol and an absorber of uv light. Hitherto, nickel isopropylxanthate (NPX) has been regarded as the most potent protective agent against light[3]; however, the rate of degradation in the presence of NPX was unchanged by the addition of uv absorber and the mixture of bis-phenol and absorber was markedly more effective. Furthermore, the nickel salt is green, whereas the bis-phenols are relatively nonstaining.

The work described here is an evaluation of vulcanizates in which the phenol and absorber have been incorporated before cure. The phenol employed was 2,2′-methylene-bis(4-methyl-6-*tert*-butyl phenol) (Antioxidant 2246 of the American Cyanamid Co.) and the absorber was Tinuvin P (a product of undisclosed formula marketed by Geigy Ltd.), chosen since it protected better in the absence of antioxidant than two other commercial absorbers. Two types of transparent vulcanizate were examined, one being an accelerated sulfur cure and the other a dicumyl peroxide cure. The recipes were as follows:

Sulfur vulcanizate.—Pale crepe 100, sulfur 2, "transparent" zinc oxide 1, TMTD 0.2, TETD 0.3, Antioxidant 2246 1, cured 20 minutes at 140° C.

Peroxide vulcanizate.—Pale crepe 100, Dicup 3, Antioxidant 2246 1, cured 60 minutes at 140° C.

Vulcanizates were prepared according to these recipes both with and without 2 parts of Tinuvin P added before vulcanization; the addition of Tinuvin P had no effect on tensile properties. The samples for examination by measurement of stress relaxation were vulcanized in a mold designed to give sheets 0.2 mm thick while the samples for exposure to sunlight were 2.5 mm thick.

Stress relaxation, which measures directly the relative amount of breakdown of the rubber network, was carried out in air at 25° C under irradiation with the light of wavelength 313 mμ and greater emitted by a high pressure mercury lamp. Tinuvin P brought about a marked decrease in the rate of degradation both in the peroxide and the sulfur vulcanizate, particularly in the latter case (Figure 1). When the protective agents were the same, the sulfur

* Reprinted from the *Journal of Applied Polymer Science*, 2, pages 367 and 368 (1959).

vulcanizate was found to be photochemically degraded far more rapidly than the peroxide vulcanizate. An auxiliary experiment, in which an antioxidant less stable in light, 2,5-di-*tert*-amylhydroquinone (Santovar A of Monsanto Ltd.), was introduced with and without Tinuvin P into a peroxide vulcanizate by swelling from ethyl acetate solution, showed that the uv absorber prolonged the life of the antioxidant as well as lowering the rate of degradation of the vulcanizate. In absence of both 2246 and Tinuvin P (removed by extraction) degradation was extremely rapid.

Similar samples both of the peroxide and the sulfur vulcanizate to those subjected to photochemical degradation were examined by stress relaxation in air at 100° C, and Tinuvin P was found to have no effect on thermal aging. The thermal aging of the peroxide vulcanizate was much better than that of the sulfur vulcanizate.

Sunlight aging of these materials was carried out in racks on the laboratory roof, with the samples facing south and at an angle of 45° to the vertical. They were exposed, unstrained, for 8 weeks in summer (approximately 400 hours sunshine). The results obtained are in accord with those obtained by stress relaxation and are illustrated by photographs (Figure 2) in which the samples have been slightly bent so as to enable the cracking pattern to be more clearly seen. After exposure the Dicup stock containing Antioxidant 2246 and

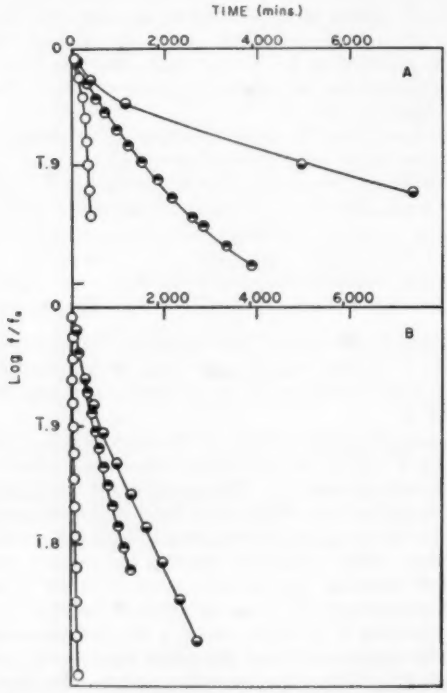

FIG. 1.—Stress relaxation at 25° C in uv light of (*A*) dicumyl peroxide and (*B*) sulfur-accelerator vulcanizates. (○) Extracted control. (◓) With 2246 only. (◒) With 2246 and Tinuvin P.

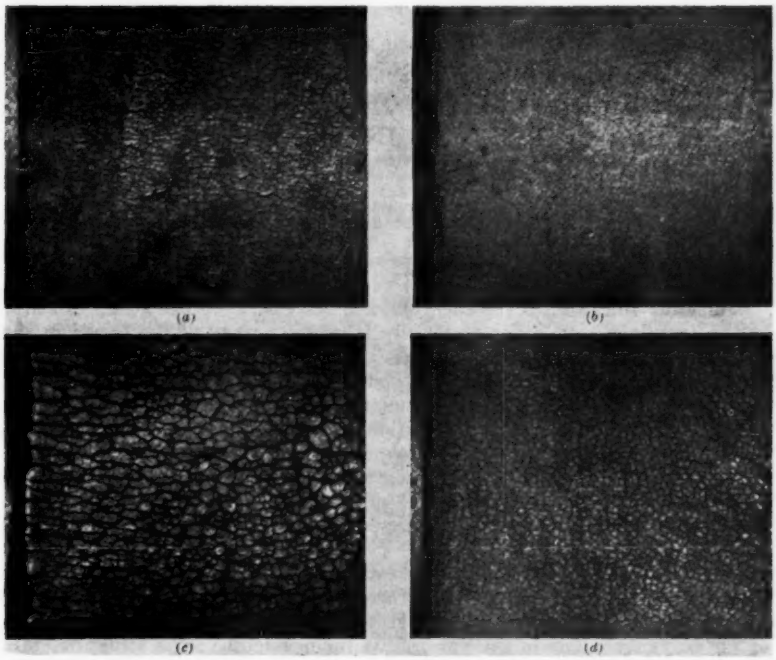

FIG. 2.—Appearance of vulcanizates after 8 weeks in sunlight. (*a*) Dicumyl peroxide vulcanizate with 2246 only. (*b*) Dicumyl peroxide vulcanizate with 2246 and Tinuvin P. (*c*) Sulfur accelerator vulcanizate with 2246 only. (*d*) Sulfur accelerator vulcanizate with 2246 and Tinuvin P.

Tinuvin P was in excellent condition, showing only slight crazing, while in absence of Tinuvin P the degree of crazing was more serious. Fine crazing of the sulfur stock occurred in presence of Antioxidant 2246 and Tinuvin P, while in absence of the absorber very pronounced crazing had occurred.

It is suggested that a combination of uv absorber and nonstaining antioxidant effectively protects transparent vulcanizates against sunlight aging. In filled stocks the absorber is not so useful since the filler itself acts as a light screen.

REFERENCES

[1] Dunn, J. R., *Trans. Inst. Rubber Ind.* **34**, 20 (1958).
[2] Dunn, J. R., following article, this issue.
[3] Karmitz, P., *Rev. gén. caoutchouc* **35**, 913 (1958).

THE DEGRADATION OF MAIN CHAINS AND CROSSLINKS IN THE AGING OF VULCANIZATES *

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In sulfur vulcanizates the energy of the bond between the atoms of sulfur in the crosslinks may differ essentially from the energy of the bonds in the main chains of the polymer since, as is known[1], the thermal decomposition of the polysulfide bonds may be brought about at considerably lower temperatures than the decomposition of the main chains. It was found by one of the present authors[2] that the thermal decomposition of the sulfur bonds brings about an inhibition of the oxidation which develops in the chains of the polymer. Consequently we must not regard the destruction of the chains and the decomposition of crosslinks as independent processes. Nevertheless the difference in the rates of destruction and decomposition is so great that these processes may be separated.

There are in the literature different views as to which elements in the structure of the vulcanizates the processes of aging extend to. Tobolsky[3] asserts that the chemical relaxation of stress is caused by oxidative destruction of the polymeric chain of the vulcanizate independently of its structure. On the other hand Watson and coworkers[4] consider that the decomposition of the lattice of the vulcanizate is the result of scission of chemical crosslinks.

In the present investigation it was established that, depending upon the composition of the vulcanizate and the conditions of the experiment, the process of aging may involve both the chains of polymer and the crosslinks, forming a three-dimensional lattice of the vulcanizates.

It is well-known that slight chemical changes cause considerable alterations in the mechanical properties, therefore in the early stages of aging, when it is still impossible to detect the reaction which has started by chemical methods, mechanical methods are sufficiently sensitive.

We investigated the chemical relaxation of stress in vulcanizates differing both in the nature of the crosslinks and in the reaction capacity of the polymeric chain in relation to oxygen.

For study we selected vulcanizates based on natural and sodium butadiene rubbers, made up to the following formulas:

I—Rubber 100 parts by weight, stearic acid 2.0, zinc oxide 5.0, phenyl-2-naphthylamine 2.0, tetramethylthiuram disulfide 3.0.

II—Rubber 100 parts by weight, stearic acid 2.0, zinc oxide 5.0, phenyl-2-naphthylamine 2.0, diphenyl guanidine 1.0, sulfur 6.0.

The investigation of the chemical relaxation of stress was carried out on a specially designed apparatus, an axial compression relaxometer[5]. Throughout the whole experiment the degree of deformation was kept constant and was

* Translated by R. J. Moseley from *Doklady Akad. Nauk SSSR* 135, 1436–8 (1960); translation 881 of RAPRA.

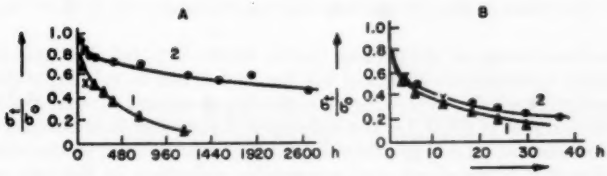

FIG. 1.—Influence of the nature of the polymer upon the kinetics of chemical relaxation of stress in vulcanizates containing predominantly monosulfides (A) and polysulfides (B). *1*—Vulcanizate based on natural rubber; *2*—Vulcanizate based on SKB.

equal to 30% compression. Before the beginning of the experiment the specimens in the deformed state were kept for 2 days at room temperature to remove physical relaxation.

In Figure 1 we present data on the kinetics of chemical relaxation of stresses in vulcanizates based on natural and sodium butadiene rubbers with predominant content of monosulfide bonds. The kinetic curves of these vulcanizates with the exception of the quite small initial portion, are described by the equation of monomolecular reaction ($\sigma_t = \sigma_0 e^{-kt}$), which is evidence of the decomposition of one type of bond. The rate constants of the process, calculated from the above equation are $1.54 \cdot 10^{-3}\ h^{-1}$ for vulcanizates of natural rubber, and for a vulcanizate of SKB $2.1 \cdot 10^{-4}\ h^{-1}$. Thus the process of chemical relaxation in vulcanizates of natural rubber takes place approximately 8 times as rapidly as with the corresponding vulcanizate of sodium butadiene rubber. It is known[2] that at the same temperature the rubbers in question differ in rate of oxidation approximately by 7 times. The rate of chemical relaxation of these vulcanizates is sharply reduced when the experiments are carried out in a vacuum (Figure 2). The lowering of the concentration of oxygen from the atmospheric level to 10^{-2} mm mercury column leads to a 5-fold reduction in the rate of the process. These facts are evidence that chemical relaxation in the present case is determined by oxidative decomposition of the polymeric chains in vulcanizates.

A quite different picture is observed in the investigation of the chemical relaxation of stresses in vulcanizates with a predominant content of polysulfide bonds.

The agreement of the exponential dependence in the present case is observed

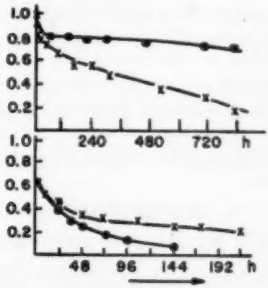

FIG. 2.—Influence of concentration of oxygen upon the kinetics of chemical relaxation of a vulcanizate based on natural rubber, containing predominantly monosulfide bonds (A) and polysulfide bonds (B). Temperature of compression (B) 90°. Temperature of aging 100° C, the degree of compression 30%. *1*—in air; *2*—in vacuum (10^{-2} mm mercury column).

only after the stress in the vulcanizate falls approximately to 50% of the original value.

In the initial stage of the process (as far as the 50% fall in stress) the rates of relaxation of stress are identical for the two types of rubber, while in the final stage they are $4.2 \cdot 10^{-2}\ h^{-1}$ for vulcanizates of natural rubber, and $3.1 \cdot 10^{-2}\ h^{-1}$ for vulcanizates of SKB, i.e. the difference in the rates does not exceed 20%. For vulcanizates of this type carrying out the experiments in the absence of oxygen does not bring about any perceptible reduction in the rate of stress relaxation of the vulcanizates as compared with the corresponding experiments carried out in air.

It must be pointed out that the decomposition of the polysulfide bonds depends little upon the concentration of oxygen and proceeds immeasurably more rapidly than the oxidative decomposition of the main chains of the polymer. The rate of chemical relaxation in air for a vulcanizate based on natural rubber with polysulfide bonds is 20 times as high as the corresponding rate for vulcanizates with monosulfide bonds. In the vulcanizates in question oxidative destruction of the polymer chain is not able to develop or lead to any perceptible fall in stress in comparison with the thermal decomposition of the polysulfide bonds, and therefore the reaction capacity of the polymers and the concentration of oxygen exert no important influence upon the rate of chemical relaxation.

On analyzing the data given, it is possible to draw the following main conclusions. In the process of aging two concurrent tendencies are observed: oxidative destruction of the main chains of the polymer and thermal decomposition of the sulfur crosslinks.

Where strong crosslinks (monosulfides) are present in the vulcanizates the chemical relaxation of stress is determined by the oxidative destruction of the main chains of the polymer, and it is therefore natural that the rate of relaxation depends upon the reaction capacity of the polymers and upon the concentration of oxygen.

In the case of the lattice of the vulcanizates being formed by polysulfide bonds, the rate of thermal decomposition of these bonds exceeds by one order the rate of oxidative destruction of the polymeric chains and determines the rate of the process of chemical relaxation of stress.

Comparison of the data on the alteration in the equilibrium modulus (the magnitude of which is proportional to the density of crosslinks) and the relaxation of stress in the process of aging of the vulcanizates in question showed that with a fall in stress to zero the equilibrium modulus alters by 15 to 20% at the outside. This is evidence that in aging in the stressed state there takes place not only decomposition of the bonds but also a further regrouping. It is natural that the destruction of bonds takes place in stressed places, and the formation of new bonds in unstressed portions of the lattice. As a result of such regrouping we observe a gradual reduction in the number of stressed bonds to the point of their complete exhaustion, while the total number of bonds remains close to the initial.

REFERENCES

[1] Dogadkin, B. A. and Tarasova, Z. N., *Kolloid Zhur.* **15**, 347–60 (1953); Rubber Chem & Technol. **27**, 838–98 (1954).

[2] Kuzminskiĭ, A. S., Leshnev, N. N. and Zuev, Yu. S., "Oxidation of Raw and Vulcanized Rubber" (book in Russian), 1957.

[3] Tobolsky, A., *J. Appl. Phys.* **27**, No. 7, 673–85 (1956); Tobolsky, A., *J. Polymer Sci.* **25**, No. 111, 494–7 (1957).

[4] Berry, J. and Watson, W. F., *J. Polymer Sci.* **18**, No. 88, 201 (1955); Watson, W. F., *J. Polymer Sci.* **25**, No. 111, 493–4 (1957).

[5] Lyubchanskaya, L. I., Shlyakhman, A. A., and Kuzminskiĭ, A. S., *Kauchuk i Rezina* **16**, No. 2, 31–3 (1957).

INTERNAL RUPTURE OF BONDED RUBBER CYLINDERS IN TENSION *

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1. INTRODUCTION

An unusual rupture process has been encountered in the course of an experimental examination of the tensile strength of vulcanized rubber cylinders, bonded to plane metal endpieces. It consists of the sudden appearance of internal flaws at a well-defined, and comparatively small, tensile load. Their occurrence may be marked by a discontinuity in the curve relating the applied tensile load to the deflection, and sometimes by an audible popping, while in particularly weak rubbers they may cause complete failure. In general the flaws are wholly enclosed and might well pass undetected, although their presence would be expected to impair the strength, service behavior and life.

An experimental study of the cracking process is described in Sections 2 and 3 below. A theoretical treatment is given in Section 4.

Yerzley[1] has described a 'yield-point' in the load-extension relations of similar testpieces and attributed it to internal rupture. Where comparison can be made, his observations are in reasonable agreement with those described below. [At the time of the original publication of this work the authors were unaware that Busse had described the phenomenon of internal rupture (*J. Appl. Phys.* **9**, 438 (1938)), in addition to, and slightly earlier than, Yerzley. Advantage is taken of the present opportunity to acknowledge Busse's work.]

2. EXPERIMENTAL METHOD

Measurement of cracking load.—The testpieces consisted of vulcanized rubber cylinders, bonded to plane metal endpieces by means of cements (Ty-Ply UP and RC) during vulcanization. The cylinders were generally 2 cm in diameter and from 0.06 to 0.5 cm in thickness. Many different rubber formulations were employed, those to which particular reference is made below being given in the Appendix.

The load-deflection relations in tension were determined using a Hounsfield tensometer, the rate of deflection being adjusted to about 100% of the testpiece thickness per minute. Some typical experimentally determined relations are shown in Figure 1 for testpieces of various thicknesses of a soft natural rubber vulcanizate D.

The point at which cracking occurred was, in general, clearly shown by a marked discontinuity in the load-deflection relation, accompanied frequently by an audible popping. As the testpiece thickness increased, however, the change in character of the load-deflection relation became much less pro-

* Reprinted from the *Proceedings of the Royal Society*, Vol. 249*A*, pages 195–205 (1958). See also *Nature* **180**, 912 (1957); RUBBER CHEM. & TECHNOL. **31**, 393 (1958). The present address of Dr. Gent is University of Akron, Akron, Ohio.

nounced, although small fluctuations in the measured load, which are not resolvable in the corresponding curves of Figure 1, were observed when a critical value of load was exceeded. Such behavior was also observed generally for testpieces of rubber containing large quantities of carbon black. The maximum value of the tensile load attained before the first fluctuation, which ranged from a marked fall to a slight momentary stoppage, has therefore been taken as a characteristic cracking load. This definition yielded unambiguous, highly reproducible values, indicated in Figure 1 by small arrows.

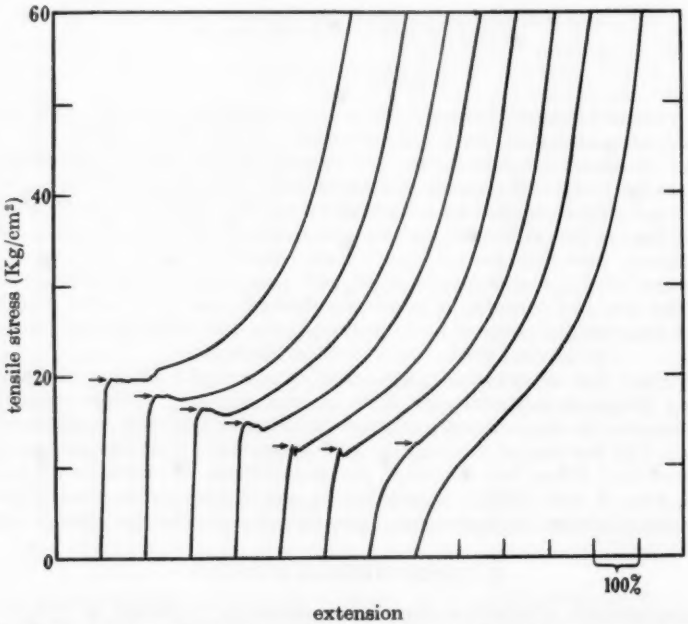

FIG. 1.—Experimentally determined load-extension relations for bonded rubber cylinders of vulcanizate D. Testpiece dimensions: diameter, 2.0 cm; thickness (from left to right), 0.056, 0.086, 0.145, 0.183, 0.320, 0.365, 0.565, 0.980 cm.

A number of testpieces of vulcanizate D were cut open after the imposition of various tensile loads. No sign of internal flaws was found for loads smaller than the cracking load defined above, while for loads slightly exceeding this, well-defined cracks were found to be present. For loads much higher than the cracking load secondary cracks were found, particularly in the neighborhood of the bonded surfaces, but the main crack pattern was not greatly altered. The cracking load defined above may therefore be considered appropriate to the main cracking process.

Evidence for crack formation at critical load.—Three further experiments were carried out to confirm that the change in character of the load-deformation relation is associated with the formation of internal flaws. In the first, a testpiece of vulcanizate D was subjected to a loading and unloading cycle with a maximum imposed tensile load somewhat larger than the characteristic cracking

load. The corresponding load-deflection relation is shown in Figure 2, Curves I and II. The testpiece was then extended again (Curve III) and was found to follow closely the unloading Curve II, markedly below Curve I, suggesting that an irreversible softening had occurred on the first extension. As the soft natural rubber vulcanizate used resembles an ideal highly elastic material, the irreversibility cannot be attributed to hysteresis and is evidence therefore for internal failure.

In a second experiment, photographs were taken of a testpiece in the unstrained state, subjected to a load of 54 kg, and subjected to a load of 59 kg. The cracking load for this testpiece was about 58 kg. From measurements on the photographed silhouettes of the testpiece its volume was calculated in the three states, and was found to increase by only 1% or so under the load of 54 kg but by a further 7% under the additional 5 kg, suggesting the formation of internal voids.

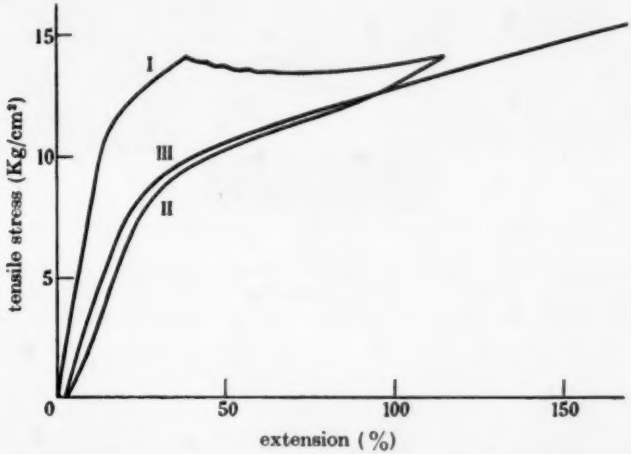

FIG. 2.—Load-extension relations for a cylinder of vulcanizate D, 2.0 cm in diameter and 0.19 cm thick. Curve I, first extension; Curve II, retraction after first extension; Curve III, second extension.

In a third experiment a testpiece was prepared in a transparent vulcanizate G and subjected to increasing tensile loads. At the characteristic cracking load a relatively large hole appeared in the center of the testpiece. As the deflection increased further, the load remaining substantially constant, other flaws occurred until the testpiece appeared to consist principally of large voids. On releasing the testpiece they reduced to cracks of the size and number usually encountered. A photograph of the stretched testpiece under a tensile stress of 8.6 kg/cm² is shown in Figure 3, the large central hole being indicated by an arrow. The circumferential mark round the testpiece is merely the mold-dividing line and serves to show that the void is entirely enclosed.

3. EXPERIMENTAL RESULTS

Crack size, number, and disposition.—Testpieces of vulcanizate D, similar to those for which the load-deflection relations are given in Figure 1, were subjected to a tensile stress of 28 kg/cm² and then cut open. The central cross

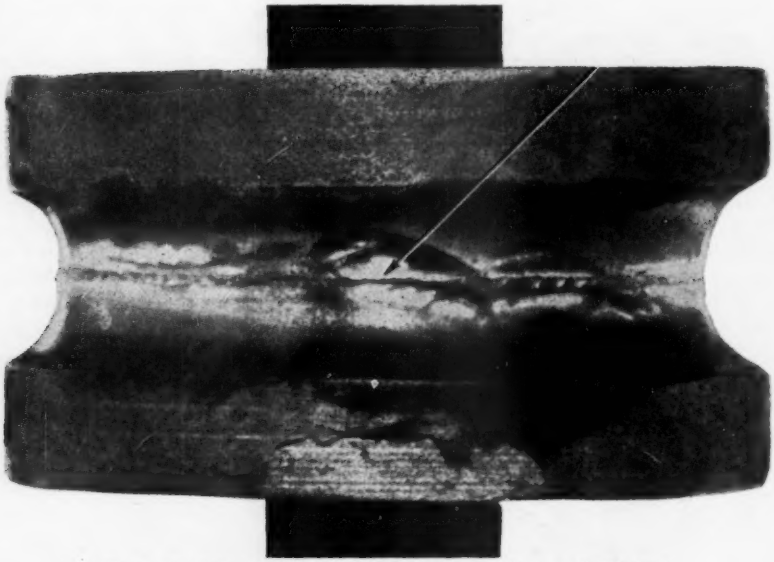

FIG. 3.—Bonded cylinder of vulcanizate G under a tensile stress of 8.6 kg/cm².

sections are shown in Figure 4. In the thinner testpieces a large number of small cracks was found, uniformly distributed across the section but ceasing in the neighborhood of the free surface. As the testpiece thickness increased

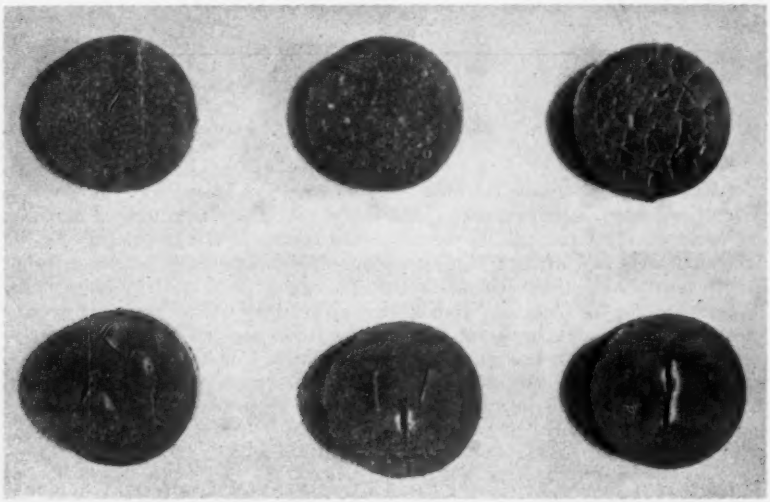

FIG. 4.—Central cross sections of testpieces of vulcanizate D, cut open after the imposition of a tensile stress of 28 kg/cm². The testpiece thicknesses are: top row, left to right, 0.061, 0.089, 0.137 cm; bottom row, left to right, 0.180, 0.295, 0.370 cm.

the average crack size became larger and the number decreased until only one or two large cracks occurred in the center of the testpiece.

When the thickness was greater than about 0.5 cm the cracks were found to occur in two regions near the two metal endpieces, the central portion of the testpiece being free from cracks. Testpieces of this thickness do not exhibit marked curvature or necking over the whole free surface; it is confined to regions close to the bonded faces, the central region being relatively uniformly extended. It seems probable that the cracking is associated with the necking of the testpieces under tensile loads, and a theoretical treatment on this basis is presented in Section 4.

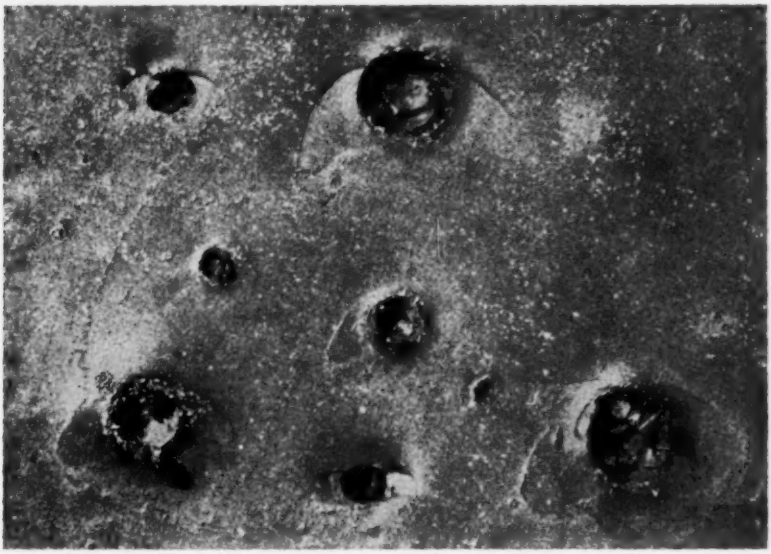

FIG. 5.—Central cross section of a testpiece of a vulcanizate containing carbon black (lampblack), cut open after the imposition of a large tensile load. (Magn. × 13.)

Cracking in carbon black-filled vulcanizates.—Similar behavior was shown by testpieces of vulcanizates containing carbon black. The cracks were found to be of quite a different appearance, however, when large quantities of carbon black were present, being generally spherical with marked 'onion-skin' features as shown in Figure 5. The difference between the flaws formed in unfilled and filled vulcanizates seems to be related to the different processes observed in linear tearing, namely, smooth and knotty tearing, respectively[2]. The spherical flaws presumably correspond to a three-dimensional form of knotty tearing.

The cracking load was found to be much less well defined for the carbon black-filled vulcanizates, presumably because of the smaller size of the flaws formed. For moderately thick testpieces it was not found possible to identify the point at which cracking occurred from observations of the load-extension relations.

Dependence of cracking stress on testpiece thickness.—In Figure 6 the mean cracking stress S', given by the tensile load at which cracking occurred divided

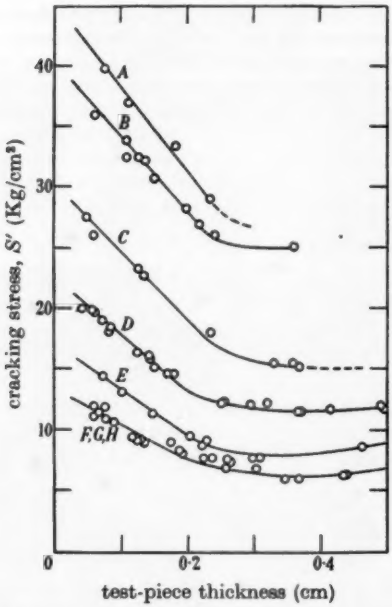

FIG. 6.—Relations between the cracking stress S' and the testpiece thickness for a number of different vulcanizates.

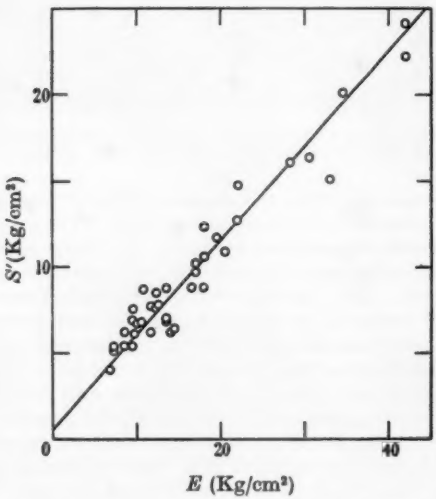

FIG. 7.—Relations between the cracking stress S' and the Young's modulus E of the vulcanizate, for testpieces 0.3 cm thick.

by the area of one bonded face, is plotted against the testpiece thickness for a number of different vulcanizates. As the testpiece thickness is increased from a very small value to 0.3 cm the cracking stress is seen to fall by about a factor of two, becoming substantially constant thereafter.

Dependence of cracking stress on stiffness and strength of the rubber.—The cracking stress S' was found to be generally higher for the stiffer vulcanizates, depending linearly on the Young's modulus E of the rubber to a first approximation. The measured values of S' for testpieces about 0.3 cm thick are plotted in Figure 7 against the values of E, calculated from measurements of the British Standard hardness[3], for all the rubbers examined. The full line shown in Figure 7 represents the relation

$$S' = 0.55E + 0.5 \text{ kg/cm}^2$$

and is seen to describe the experimental measurements with fair success. It is compared with the predictions of the theoretical treatment in Section 4.

TABLE I

REPRESENTATIVE VALUES OF BREAKING STRESS

Vulcanizate	Hardness (B.S. degrees)	Young's modulus (kg/cm²)	Cracking stress (kg/cm²) for testpieces 0.3 cm thick	Average breaking stress (kg/cm²)
A	70	60	28.7	106
B	63	42	25.2	113
C	55	28.5	15.9	103
D	45	18.0	12.3	66*
E	38	12.8	8.0	12.5
F	37	12.2	7.7	12
G	33	10.0	6.7	39.5*
H	32	9.5	6.95	34*

* Failure at the rubber/metal interface.

The tensile strength of the rubber employed was found to have only a minor effect on the value of cracking stress obtained. For example, soft vulcanizates of natural rubber and a butadiene-styrene copolymer (SBR) of similar stiffness were found to have similar cracking stresses of 8.5 and 7.6 kg/cm², respectively. The tensile strengths of the rubbers were quite dissimilar, however, being 158 and 20 kg/cm², respectively, calculated on the unstrained cross-sectional area.

Ultimate strength of bonded testpieces.—The majority of testpieces failed ultimately at a value of applied stress many times larger than the cracking stress. Representative values are given in Table I. For a number of particularly weak vulcanizates, however (for example, vulcanizates E and F in Table I) total failure occurred consistently at a load only slightly higher than the cracking load. The fractures appeared to be due to the growth of one or two internal cracks to sever the testpiece.

4. THEORETICAL TREATMENT

Effect of testpiece thickness.—A treatment has been given elsewhere for the stiffness of bonded rubber cylinders under small *compressions*[4, 5]. The compressive stress is resolved into two components, one arising from a homogeneous

compression of the cylinder and one arising from the restraints at the bonded surfaces. The second component, the major one for short cylinders, has been shown to consist of a hydrostatic pressure having a maximum value P_m at points along the axis of the cylinder, given by

$$P_m = Eea^2/h^2$$

where E is the Young's modulus of the rubber, e is the fractional compression imposed, and a and h are the radius and thickness of the cylinder, respectively. The average compressive stress S necessary to maintain the compression e has been obtained as

$$S = Ee(1 + a^2/2h^2)$$

Hence

$$S = \tfrac{1}{2}P_m(1 + 2h^2/a^2) \tag{1}$$

Similar relations will govern the behavior of bonded cylinders under small extensions, where P_m now denotes the negative hydrostatic pressure acting at the axis of the cylinder when a small extension e is imposed.

It is assumed that the cracking process described in preceding sections consists of the formation of local fractures under the action of a critical value of the negative pressure, denoted P'_m. The corresponding critical value S' of the applied tensile stress is obtained from Equation (1) as

$$S' = \tfrac{1}{2}P'_m(1 + 2h^2/a^2) \tag{2}$$

When the testpieces are extremely thin, however, the deformation will consist substantially of a bulk dilatation. The negative hydrostatic pressure P_m will then be uniform throughout the testpiece, and its value will be given by the imposed tensile stress S.

It follows that, if cracking occurs at a critical value P'_m of the negative hydrostatic pressure, the corresponding cracking stress S' will decrease from a value of P'_m for infinitesimally thin testpieces to a value of about $P'_m/2$ for testpieces of moderate thickness. This variation is in accord with that observed experimentally, Figure 6.

Moreover, the critical value of P'_m will be attained over the major part of the cross-section for the thinner testpieces, whereas it will be attained only in the central region of moderately thick testpieces. A corresponding change in the location of cracks is observed, those in the thinnest testpieces being distributed throughout the cross section, while those in moderately thick testpieces are restricted to the central region, Figure 4.

It has been found experimentally that the cracking stress is linearly dependent on the Young's modulus of the vulcanizate, to a first approximation, Figure 7. For testpieces of about 0.3 cm thickness the relation obtained was

$$S' = 0.55E + 0.5 \text{ kg/cm}^2$$

For these testpieces the critical negative hydrostatic pressure P'_m is given by Equation (2) above as 1.7 S', and hence

$$P'_m = 0.94E + 0.85 \text{ kg/cm}^2$$

A similar relation would have been obtained by considering the cracking stress for extremely thin testpieces, since the cracking stress observed is about twice as large, while it is also a direct measure of P'_m.

In the following section relations between P'_m and E are derived theoretically.

Calculation of cracking stress.—The behavior of a small region of the testpiece under the action of a negative hydrostatic pressure P_m is considered below. The region is assumed to contain an extremely small spherical cavity, sufficiently small for the region around it to be treated as an infinitely thick spherical shell. The surface of the cavity is assumed to be force-free, and the deformation of this surface is examined when outwardly-directed tractions of magnitude P_m act on the outer surface, i.e., at infinity.

Solutions may be obtained, when a particular form is assumed for the stored-energy function of the rubber, for the deformation of a thick spherical shell under the action of forces applied to the inner and outer surfaces[6]. For an incompressible highly elastic material which is isotropic in the undeformed state, the stored energy W is a function of two strain invariants I_1 and I_2, where

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_1^{-2}\lambda_2^{-2}$$
$$I_2 = \lambda_1^{-2} + \lambda_2^{-2} + \lambda_1^2\lambda_2^2$$

and λ_1, λ_2 are the principal extension ratios. The kinetic theory of rubberlike elasticity yields a particularly simple form for the stored-energy function with no term involving I_2,

$$W = C(I_1 - 3)$$

where C is a constant. When the spherical shell is infinitely thick and the inner surface is force-free, the corresponding relation between the extension ratio λ of the circumference of the inner surface and the tractions P_m acting at infinity takes the form

$$P_m = C\left(5 - \frac{4}{\lambda} - \frac{1}{\lambda^4}\right) \tag{3}$$

A relation between P_m and λ may also be obtained when the stored-energy function for the rubber takes the two-constant Mooney form[7]. However, the rubber at the surface of the cavity is in two-dimensional extension, a deformation for which the Mooney form of stored-energy function is quite inappropriate[8, 9]. A simple logarithmic form for the stored-energy function,

$$W = W_1(I_1 - 3) + W_2 \ln (\tfrac{1}{3}I_2)$$

where W_1 and W_2 are constants, has recently been proposed as generally applicable[9], the corresponding relation between P_m and λ being

$$P_m = W_1\left(5 - \frac{4}{\lambda} - \frac{1}{\lambda^4}\right) + \frac{W_2}{3} \times \left[\ln\left(\frac{3\lambda^6}{2+\lambda^6}\right) + 2\sqrt{2}\left\{\tan^{-1}\sqrt{2} - \tan^{-1}\left(\frac{\sqrt{2}}{\lambda^3}\right)\right\}\right] \tag{4}$$

where W_1 and W_2 are constants. Experiments indicate that the value of the ratio W_2/W_1 is of the order of 1.0 for a soft vulcanized rubber, and it has been

given this value in the following analysis. The conclusions are not materially affected, however, if widely different values are assumed.

In Figure 8 the predictions of Equations (3) and (4) are represented by Curves I and II, respectively, the negative hydrostatic pressure P_m being plotted relative to the Young's modulus E against the extension ratio λ at the surface of the cavity. For the kinetic theory form of stored-energy function E is given by $6C$, while for the logarithmic form E is given by $6W_1 + 2W_2$.

The two relations are seen to be closely similar in form. They both predict a limiting value for P_m at which λ becomes infinite, i.e., the cavity becomes infinitely large. The limiting values are 0.833 E and 0.783E, respectively, in fairly good agreement with the experimentally determined relation for the

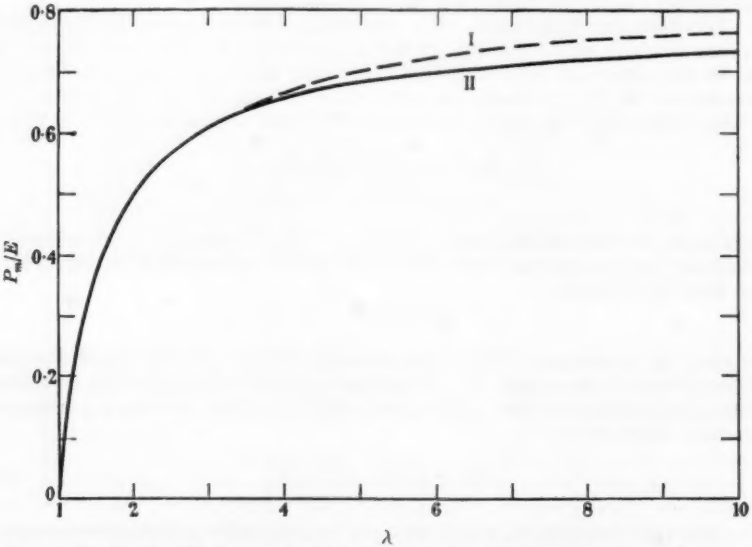

FIG. 8.—Calculated relations for an infinitely thick spherical shell between the outwardly-directed tensile stress P_m, acting at infinity, and the extension ratio λ of the inner circumference of the shell. Curve I, simple kinetic theory; Curve II, logarithmic form of stored-energy function.

critical negative hydrostatic pressure for crack formation, namely $P'_m = 0.94E + 0.85$ kg/cm^2. (The small constant term may be identified with the atmospheric pressure, which is of this order of magnitude and has not been taken into account in the theoretical treatment given above.)

The cavity will presumably burst open at a value of λ between about 4 and 10, given by the extensibility of the rubber in two-dimensional extension. Over this range of λ both relations predict little alteration in P_m. Effectively, therefore, both relations predict similar critical values for P_m, independent of the rubber strength or extensibility over the practicable range and directly proportional to the Young's modulus, in agreement with experiment. In view of the inadequacy of the stored-energy functions when the rubber is very highly deformed, approaching breaking elongations, the agreement between the predicted values of the hydrostatic tension P'_m for crack formation and those calculated from the measured cracking stresses must be regarded as highly satisfactory.

Once rupture of the cavity surface occurs, the tear will proceed until the stresses P_m are relieved by the growth of the void (or series of voids) to a size sufficient to reduce the hydrostatic tensions markedly. This is in accord with observation also.

A remarkable feature of the theoretical solution is that the predicted cracking stress is quite independent of the initial size of the cavity. This explains why the measured cracking stresses are found to be highly reproducible, in contrast to other fracture processes, and also the experimental observation that vulcanizates prepared from specially clean rubber and smoked sheet rubber with small quantities of fine sand added show similar cracking stresses.

For sufficiently small cavities, however, it would presumably be necessary to consider surface energy changes, as in classical cavitation theory, in addition to the treatment developed above from the theory of large elastic deformations. The general agreement obtained without including such terms suggests that cavities of relatively large size already exist in vulcanized rubber, possibly caused by the presence of inclusions—for example, particles of dust or impurities in added materials.

5. GENERAL CONCLUSIONS

It has been shown that comparatively small tensile loads cause internal rupture in bonded rubber cylinders. A series of small cracks is formed in extremely short cylinders, uniformly distributed across the section. In moderately thick cylinders only one or two large cracks form in the center, while in relatively tall cylinders the cracks occur only in the neighborhood of the bonded surfaces.

The cracks appear to form in all vulcanizates although their size and shape are affected by the properties of the rubber. In particularly weak rubbers they may lead to early failure, at loads which are much below the expected breaking load. Their appearance may also lead to major changes in the load-deflection relationship of the unit, and would be expected to impair the strength, service behavior and life.

The stress at which the cracks form has been found to be highly reproducible. It decreases as the testpiece thickness is increased from very small values, becoming substantially constant for moderately thick specimens. At any thickness it has been found to depend linearly on the Young's modulus of the rubber, to a first approximation, and to be virtually independent of the rubber strength or extensibility.

The observed variation of cracking stress and crack disposition with testpiece thickness has been shown to be in accord with a proposed rupture criterion —that the negative pressure component of the applied tensile stress reaches a critical value.

Solutions for the expansion of a small spherical cavity in an infinite block subjected to a negative pressure have been obtained by means of the theory of large elastic deformations. They predict a critical negative pressure at which the cavity becomes infinitely large. The calculated value is in satisfactory agreement with the experimental measurements of cracking stress, and the observed linear dependence on the Young's modulus of the vulcanizate is predicted. The observation that the cracking stress is virtually independent of the extensibility or strength of the rubber is also shown to be in accord with the theory, and the good reproducibility is accounted for. The experimental results thus suggest that the proposed criterion for crack formation is correct.

SUMMARY

An unusual rupture process is described. It consists of the sudden appearance of internal cracks in bonded rubber cylinders at a well-defined and comparatively small tensile load. The cracks occur in all the vulcanizates examined, and in particularly weak rubbers are found to cause failure. Their appearance may also lead to marked changes in the load-deflection relationship.

A theoretical treatment is presented on the basis of a proposed criterion for crack formation. It is assumed that they form when the negative hydrostatic pressure component of the applied stress reaches a critical value. It is shown by means of the theory of large elastic deformations that a critical value of the negative pressure exists at which any cavity in the rubber will burst, and the calculated value is shown to be in satisfactory agreement with experiment. Moreover, the theory successfully predicts the observed dependence of the cracking stress on the Young's modulus of the rubber, its virtual independence of the rubber strength and extensibility, and the general form of the observed variation of cracking stress and crack disposition with the thickness of the testpiece.

ACKNOWLEDGMENTS

The authors acknowledge many helpful discussions with Mr. A. G. Thomas and the supervision and advice of Mr. W. P. Fletcher. This work forms part of a program of research undertaken by the Board of the British Rubber Producers' Research Association.

APPENDIX

The mix formulations in parts by weight and the vulcanization conditions employed are given below:

	A	B	C	D	E	F	G	H
Natural rubber (smoked sheet)	100	100	100	100	100	—	100	100
SBR (Polysar S)	—	—	—	—	—	100	—	—
Zinc oxide	5	5	5	5	—	5	—	0.5
Stearic acid	2	1	1	2	—	1	—	0.5
Zinc stearate	—	—	—	—	—	—	—	1.5
Sulfur	2.5	2.5	2.5	2.5	—	2	—	2
Dicumyl peroxide	—	—	—	—	5	—	3	—
Santocure[a]	0.7	0.7	0.6	0.6	—	0.8	—	—
Vulcafor DHC[b]	—	—	—	—	—	—	—	0.375
Phenyl-2-naphthylamine	1	1	1	1	—	1	1	—
Nonox EX[c]	—	—	—	—	—	—	—	1
Dutrex R[d]	1	—	—	—	—	—	—	—
Lampblack	55	40	20	—	—	—	—	—
Vulcanization time (min at 140° C)	30	30	30	40	50	40	50	10

[a] *N*-cyclohexyl benzthiazyl sulphenamide.
[b] Mercaptobenzthiazole + zinc diethyl dithiocarbamate.
[c] Substituted triphenyl methane.
[d] Hydrocarbon oil (processing aid).

REFERENCES

[1] Yerzley, F. L., *Ind. Eng. Chem.* **31**, 950 (1939).
[2] Greensmith, H. W., *J. Polymer Sci.* **21**, 175 (1956).
[3] Gent, A. N., *Trans. Inst. Rubber Ind.* **34**, 46 (1958).
[4] Gent, A. N., *Proc. Rubber Eng. Conf.*, Natural Rubber Development Board, London, 1956, p. 25.
[5] Gent, A. N. and Lindley, P. B., *Proc. Inst. Mech. Engrs.*, (London) **173**, 111 (1959).
[6] Green, A. E. and Zerna, W., "Theoretical Elasticity", Oxford University Press, 1954.
[7] Mooney, M., *J. Appl. Phys.* **11**, 582 (1940).
[8] Rivlin, R. S. and Saunders, D. W., *Phil. Trans.* **A243**, 251 (1951).
[9] Gent, A. N. and Thomas, A. G., *J. Polymer Sci.* **28**, 625 (1958).

THE INDENTATION AND PUNCTURE PROPERTIES OF RUBBER VULCANIZATES *

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INTRODUCTION

The relation between the applied load and the depth of penetration of rubber compounds at relatively small deformations has been examined extensively, both theoretically and experimentally. In general, the relation is a function of the shape of the indenter, and the difference between a theoretically derived relation and one obtained experimentally lies in a shape factor introduced in the latter case. For example, Timoshenko[1], using the theory of elasticity, derived the equation

$$F = 1.78\, Er^{0.5}d^{1.5} \tag{1}$$

for a ball-type indenter, whereas, Scott[2] obtained an empirical equation

$$F = 1.91\, Er^{0.65}d^{1.35} \tag{2}$$

for penetration of the sample to a depth not exceeding 80% of the indenter diameter. F, E, r and d stand for load, Young's modulus, radius of indenter and depth of penetration respectively. Thus, if one rewrites Scott's equation as

$$F = 1.91\, Er^{0.5}d^{1.5}(r/d)^{0.15} \tag{2a}$$

Equations (1) and (3) differ essentially by a shape factor which is explicitly given. For greater penetration, Scott[3] finds that Equation (2) no longer holds but that the theoretical relation of

$$F = 2.67\, Erd \tag{3}$$

originally derived[4] for a flat-ended cylindrical indenter applies.

Puncture of rubber was suggested by Vickers and Robison[5] as a means of studying the surface strength or penetration resistance of a rubber compound. They have indicated that materials which exhibit higher resistance to penetration trend toward greater abrasion resistance. In a recent study[6], the puncture strength of a number of rubber compounds was shown to vary over a wide range of rate and temperature. Upon examining the relation between the penetration force and the penetration depth, two regions of linearity were observed on a logarithmic plot of force vs. depth, see Figure 1. The force-depth relation up to puncture was found to be characteristic of all four rubber com-

* Presented at the meeting of the Division of Rubber Chemistry ACS, Louisville, Kentucky, April 19–21, 1961. Contribution No. 265 from the Research Laboratory of The Goodyear Tire & Rubber Company.

pounds studied, both gum and reinforced. The present work was undertaken to study in detail the characteristic relation between penetration force and penetration depth and to explore the puncture measurement as a method of providing useful information about rubber compounds.

EXPERIMENTAL

Shape of the indenter.—The indenter used in the present investigation is the cylindrical type with a flat end employed in the earlier work[6]. The choice of a flat-ended indenter was dictated by the reproducibility of the experimental results and the ease of fabricating and reproducing the indenters. The latter

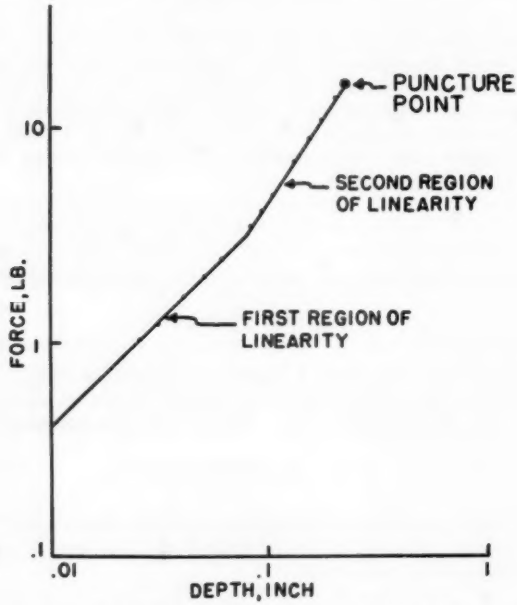

FIG. 1.—Logarithmic plot of force *vs.* depth of penetration for cold SBR tread compound at 10° C and 0.05 in./min.; diameter of indenter, 0.047 in.

reason becomes important when we bear in mind that the rubber compounds have a wide range of Young's modulus and breakage of the indenter may be unavoidable.

Size of the indenter and thickness of the rubber samples.—The mechanical strength of the indenter (q.v. range of modulus above) requires different sizes of indenter and the size of the indenter should be chosen in relation to the thickness of the rubber specimen. Scott[7] made a thorough investigation of the effect of sample thickness in different hardness tests and found that the compressive force encountered in the penetration of an elastic material can be minimized by the reduction in size of indenter for a given thickness of rubber sample. Larrick[8] has indicated that a minimum thickness of $t = 10(dD/2)^{0.5}$ is sufficient for the compressive force along the axis of penetration to drop to

TABLE I

COMPOUND FORMULAS

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X
Butyl 218	100	100									100	100												
Neoprene GNA			100	100									100	100										
Natsyn polyisoprene					100	100									100	100								
#1 ribbed smoked sheet							100	100									100	100					100	
SBR 1500									100										100	100				100
SBR 1703										100											100	100		
Sulfur	2.0	2.0			2.0	2.0	2.75	2.75	1.75	1.75	2.0	2.0			2.0	2.0	2.75	2.75	1.75	1.75	1.75	1.75	2.75	1.75
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	3.0	3.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	3.0	3.0	3.0	3.0	5.0	3.0
Magnesia			4.0	4.0									4.0	4.0										
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Mercaptobenzothiazole	0.5	0.5									0.5	0.5											0.6	
Tetramethyl thiuram disulfide	1.0	1.0									1.0	1.0												
N-oxydiethylene-2-benzothiazole sulfenamide					0.9	0.9	0.6	0.6	1.1	0.9					0.8	0.8	0.6	0.6	1.0	1.0	1.0	1.0	[illegible]	1.0
Phenyl-2-naphthyl amine																							1.0	
HAF Black											50	50	50	50	50	50	50	50	50	50	50	50		50
Regal 300 Black																							varied	
Vulcanization, min/° F	7/ 307	15/ 307	20/ 290	35/ 290	30/ 280	70/ 280	40/ 270	75/ 270	60/ 290	60/ 290	15/ 307	40/ 307	10/ 290	25/ 290	15/ 275	40/ 275	20/ 275	55/ 275	25/ 290	45/ 290	35/ 275	60/ 275	45/ 280	5/275
Radiation dosage, MR																								varied

about 1% of its initial value, d being the depth of penetration and D the diameter of the indenter. We have made an experimental study of the effect of the indenter size and the sample thickness on both the puncture strength and the puncture depth for a given rubber compound R (see Table I). The compound was cured and molded into 1 in. × 1 in. × 2 in. blocks. Two more thicknesses, 0.5 and 0.6 inches, were carefully prepared from the same 1 in. × 1 in. × 2 in. block in order to minimize any other variables such as cure time that might be involved in such a study. Three convenient sizes of indenters 0.031, 0.047 and 0.062 inches in diameter were selected. The variation in

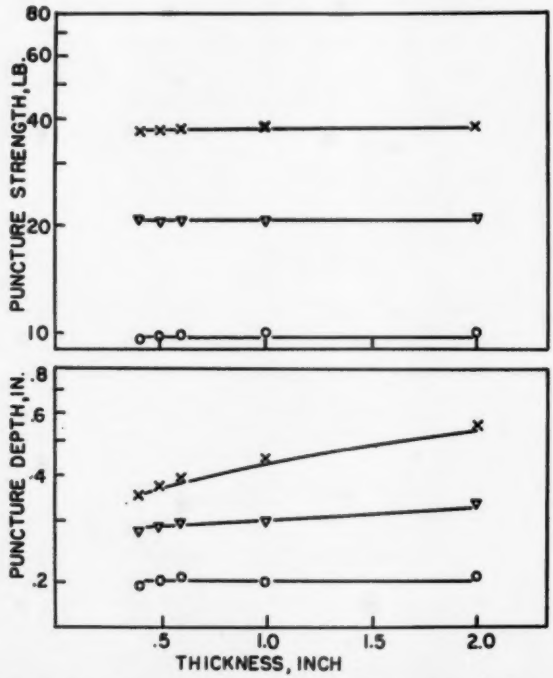

FIG. 2.—Effect of indenter size and sample thickness on the puncture strength and the puncture depth for natural tread compound R. Indenter diameters: X 0.062 in.; ▽ 0.047 in.; ○ 0.031 in.

puncture strength with thickness was found to be insignificant whereas the puncture depth did increase with thickness and the effect was most pronounced for the 0.062 in. indenter as shown in Figure 2. Therefore, the effect of thickness can be diminished by the reduction in size of the indenter, and when the minimum thickness requirement of $t = 10(dD/2)^{0.5}$ is reasonably fulfilled, this effect becomes almost negligible. For the present investigation, we chose an indenter with a diameter of 0.031 in. for the gum compounds and one of 0.047 in. diameter for the reinforced compounds as being suitable for use with the 0.5 in. × 0.5 in. × 4 in. test specimen. The effect of the test distance from a free edge was also examined. On the basis of the above considerations, a distance of $10(dD/2)^{0.5}$ should be considered necessary. However, a distance

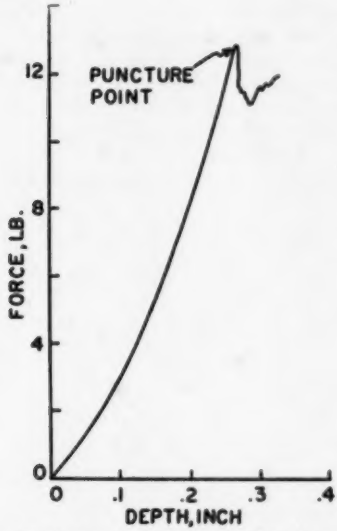

FIG. 3.—A typical penetration curve (butyl tread compound).

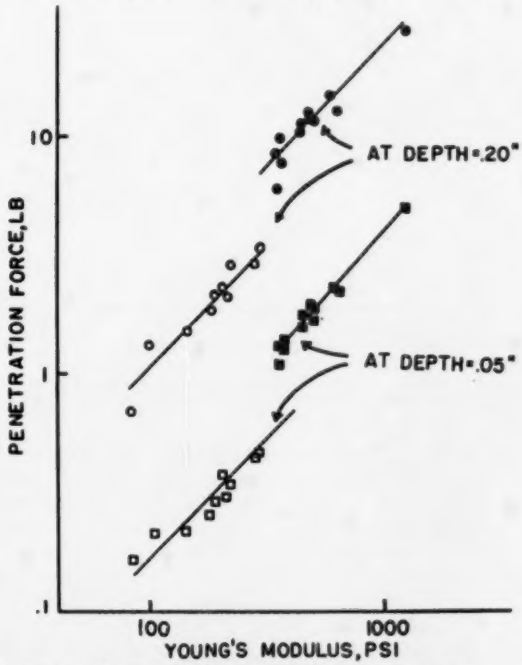

FIG. 4.—Dependence of penetration force on Young's modulus. ○, □ gum compound; ●, ■ tread compound.

of 0.25 in. was found satisfactory for the two sizes of indenter employed. A total of twenty-two rubber compounds, A to V in Table I, was selected to cover a wide range of modulus. The test specimen was placed on the compression load cell of an Instron testing machine. The indenter was mounted on the crosshead of the Instron tester directly above the test specimen. All rubber compounds were puncture-tested at a constant room temperature of 25° C and a constant rate of one inch per minute. Previous work[6] had indicated that better reproducibility of experimental results could be obtained if the indenter

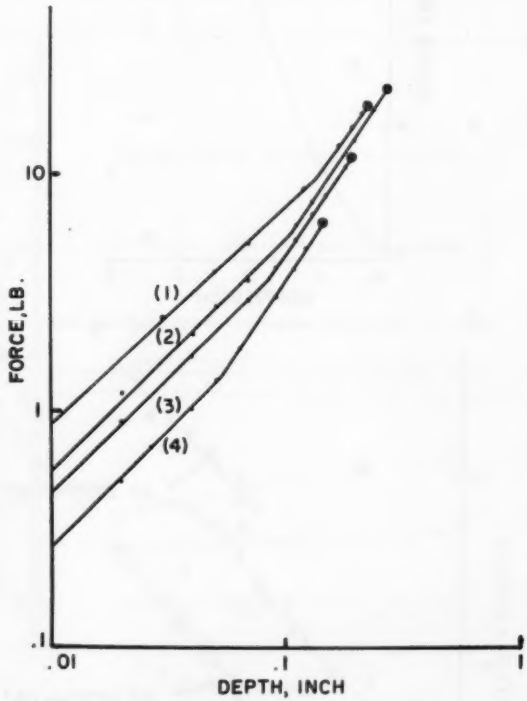

FIG. 5.—Logarithmic plot of force *vs.* depth of penetration for natural rubber tread compound R. Indenter diameters: (1) 0.078 in.; (2) 0.062 in.; (3) 0.047 in.; (4) 0.031 in.

was coated with a thin film of silicone grease before each test, and this procedure was carefully followed throughout. A minimum of two measurements was made on each compound in the evaluation of the puncture strength and depth. A typical load-depth curve is shown in Figure 3. Several sizes of indenters were also used for testing compounds R, T, and V in determining the relation between the indenter size and penetration force. In addition, Young's modulus was determined for all twenty-two rubber compounds by finding the load required to stretch a testpiece of .075 in. × 0.5 in. × 3 in. to an elongation of 15%. Standard Shore A hardness measurements also were made on the same testpieces used for puncture-testing.

RESULTS AND DISCUSSION

The force required to reach a penetration of 0.05 in., corresponding to the first region of linearity, and second, the force required to reach a penetration of 0.20 in. corresponding to the second region of linearity have been plotted against Young's modulus at 15% elongation, see Figure 4. Because of the different sizes of indenters used the gum compounds and tread compounds fall on different lines. The scattering is probably largely due to the experimental error involved in the determination of Young's modulus and the omission of the

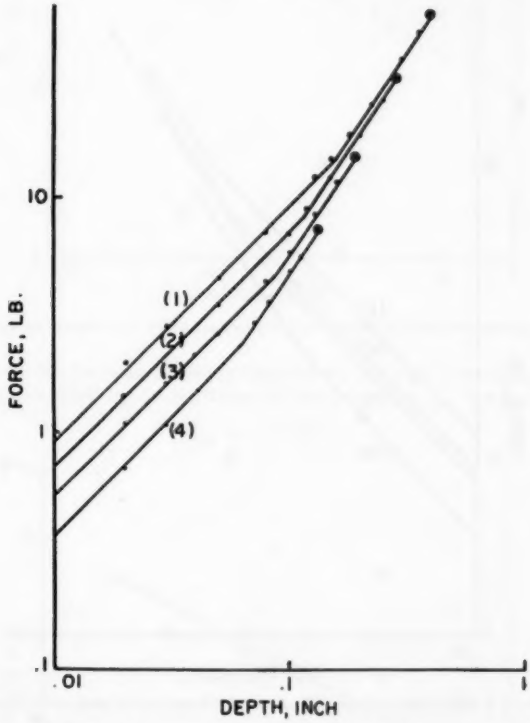

FIG. 6.—Cold SBR tread compound T; curve identifications the same as for Figure 4.

incubation time[9] in curing the rubber compounds having the 0.5 × 0.5 in. cross section. However, a slope close to one is observed for both the gum and tread compounds, indicating the direct proportionality of the penetration force to Young's modulus in both regions of linearity.

A detailed analysis of the load-depth curves obtained by puncturing compounds R, T, and V with several sizes of indenters was made by plotting the logarithm of the force *vs.* the logarithm of the depth as shown in Figures 5, 6 and 7. In the cases of compounds R and V, punctures occurred at values smaller than that expected for the 0.078 in. diameter indenter. This may be explained on the basis of minimum thickness requirement, which is far from

being fulfilled for the 0.078 in. diameter indenter. The linearity can still be observed here, and both regions of linearity show up distinctly for all four indenters. It is interesting to note that the breaks in the curves are displaced by an amount roughly proportional to the indenter diameter.

The first regions all extend to a penetration depth approximately equal to twice the indenter diameter up to which the slope is close to one for all three compounds. The force intercepts at $d = 0.01$ in., are in direct proportion to the diameters of the indenters, although there is some doubt about the lowest

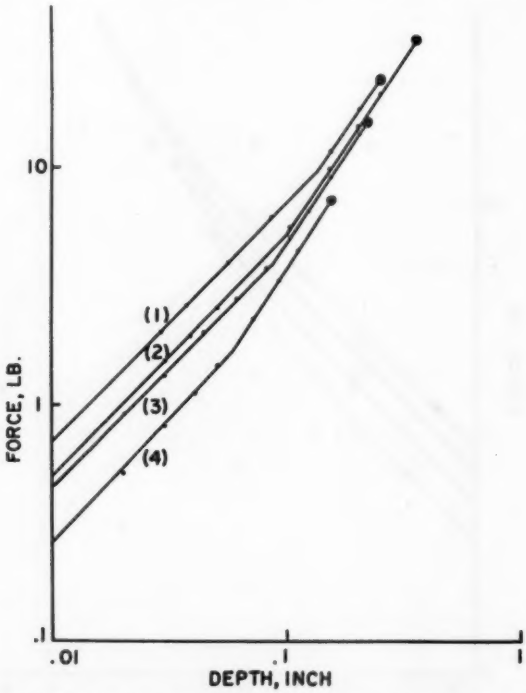

FIG. 7.—O E SBR tread compound V; curve identifications the same as for Figure 4.

points which could not be determined so accurately. Based on the experimental data shown in Figure 4, the constant in Timoshenko's equation (Equation 3) has been obtained and found to deviate by ±20% from the theoretical value. Therefore, using I to designate the first region of linearity, Equation 3 can be written as

$$F_{\mathrm{I}} = 2.67\ Erd \tag{3a}$$

which is shown to be applicable here to a first approximation. Scott[10] has also verified this theoretical relation for a flat-ended cylindrical indenter. However, he did not specify exactly what the penetration limitation was.

In the second region, the slopes are close to 1.5 and since the force has

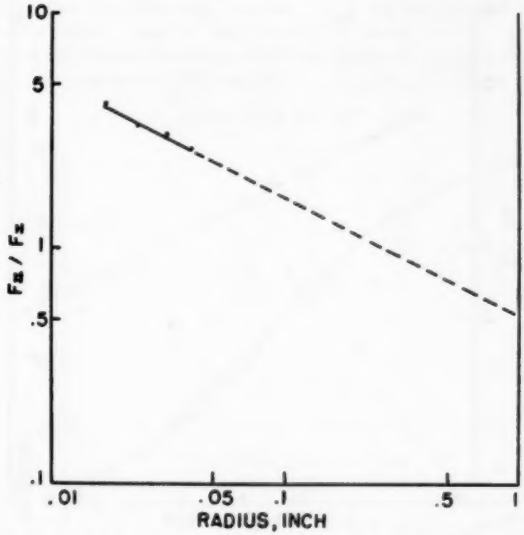

FIG. 8.—Logarithmic plot of F_{11}/F_1 vs. indenter radius for natural rubber tread compound R.

already been shown to be in direct proportion to Young's modulus, the second region can be described by an equation of the type,

$$F_{11} = cEr^m d^{1.5} \tag{4}$$

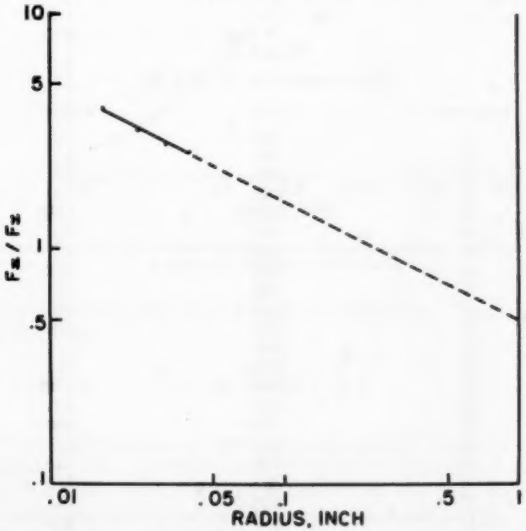

FIG. 9.—Same type of plot as Figure 8 but for cold SBR tread compound T.

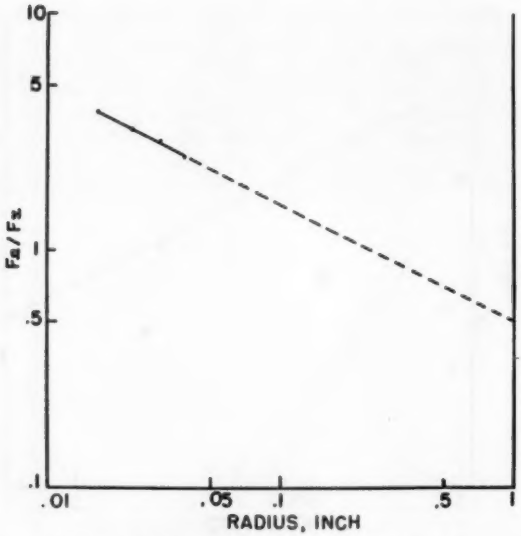

FIG. 10.—Same type of plot as Figure 8 but for O E SBR tread compound V.

where c and m are constants to be evaluated. Combining equations (3a) and (4) and extrapolating to $d = 1$, the ratio of the force intercepts is

$$F_{II}/F_{I} = c/2.67\ r^{m-1}$$

TABLE II

COMPARISON OF E_I AND E_{II}

Compound	E_I, psi	E_{II}, psi
A	83	46
B	95	112
C	224	217
D	252	256
E	120	148
F	143	172
G	157	161
H	202	282
I	169	171
J	110	113
K	414	416
L	545	548
M	700	714
N	1590	1320
O	430	431
P	570	640
Q	560	614
R	720	750
S	707	712
T	830	845
U	502	456
V	670	675

From the slope and the intercept as $r = 1$ of a log-log plot of F_{II}/F_I *vs.* the radius of the indenter, c and m can readily be shown to be 1.34 and 0.5, see Figures 8, 9 and 10, where the slopes are approximately -0.5 and the intercepts at unit radius vary between 0.49 and 0.51. We can, therefore, write

$$F_{II} = 1.34\, Er^{0.5}d^{1.5} \tag{5}$$

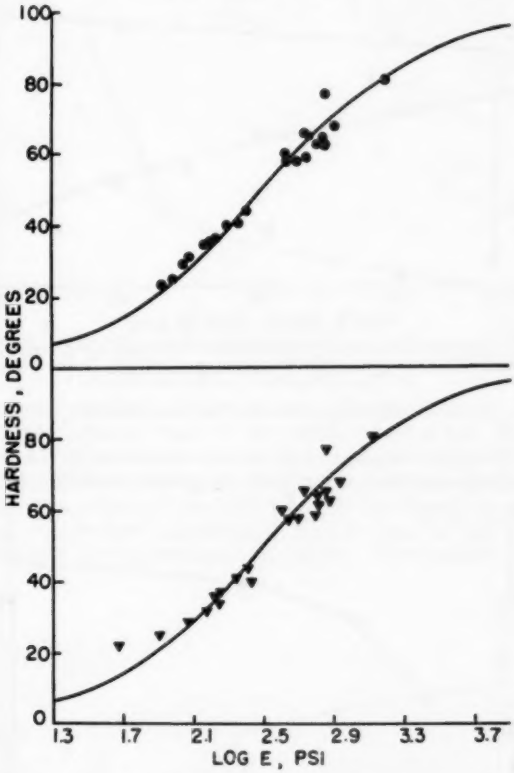

FIG. 11.—Relation between hardness and Young's modulus. ● region I; ▲ region II; full curve, theoretical.

as suitable for describing the second region of linearity. This equation can be rewritten in the form

$$F_{II} = 2.67\, Erd\left(\frac{d}{4r}\right)^{0.5} \tag{5a}$$

and $(d/4r)^{0.5}$ looked upon as a shape factor introduced in the original equation. The two equations that describe the two regions of linearity become the same when $(d/4r)^{0.5}$ is equal to unity. In other words, the first region should end when the penetration reaches about twice the diameter of the indenter, which is exactly the case observed for all four indenters.

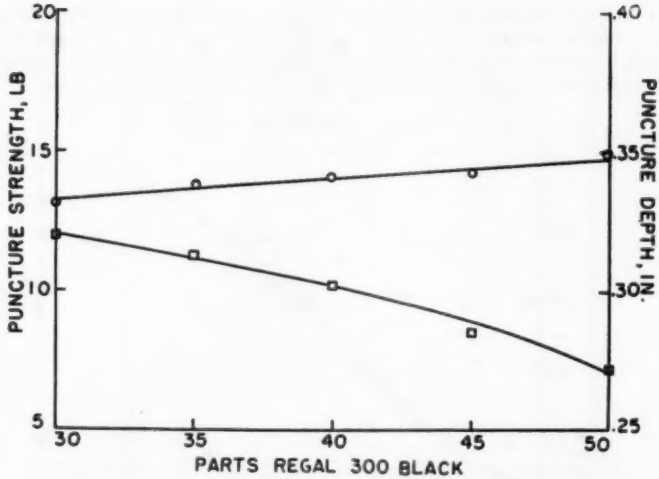

FIG. 12.—Effect of carbon black loading on puncture strength and puncture depth for natural rubber tread compound W. ○ puncture strength, □ puncture depth.

By means of the empirically derived relation between puncture strength, puncture depth, and indenter radius, the Young's modulus of rubber can also be calculated from the results of a puncture measurement. A comparison of Young's modulus calculated using both equations, namely, (3a) and (5), is

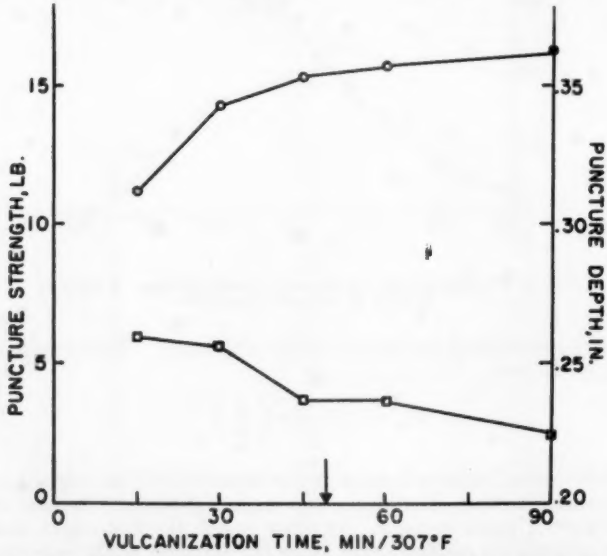

FIG. 13.—Effect of vulcanization time on puncture strength and puncture depth for butyl tread compound. ○ puncture strength, □ puncture depth.

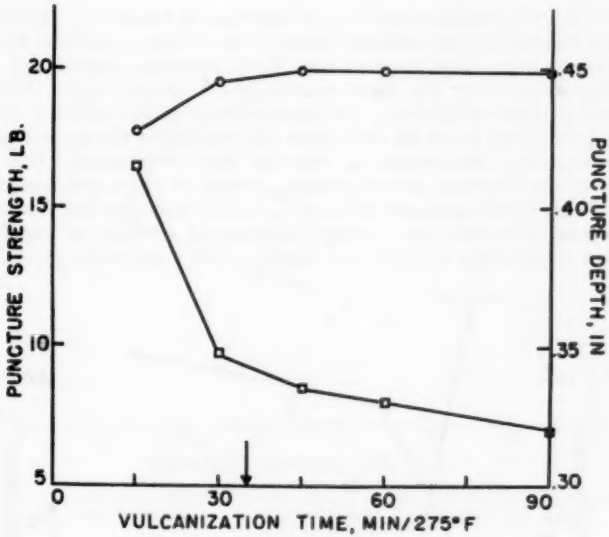

Fig. 14.—Natural rubber tread compound.

presented in Table II for all twenty-two rubber compounds. For Equation (3a) an arbitrary depth of 0.05 in. was chosen for simplicity of calculation and in Equation (5) the ultimate puncture strength and depth were employed. The agreement is considered surprisingly good in spite of the experimental errors involved and the approximations made. The Young's modulus so

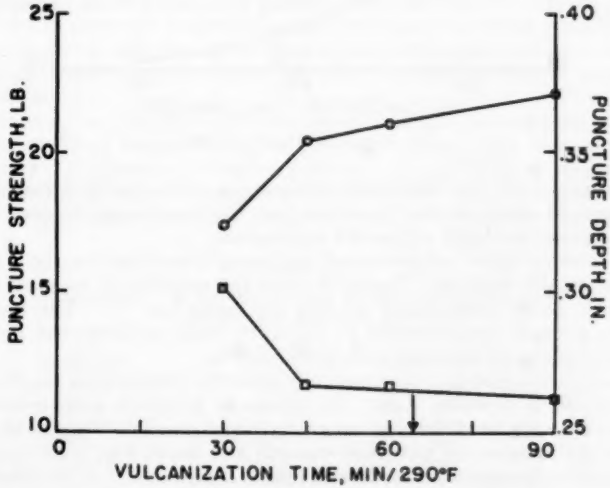

Fig. 15.—Cold SBR tread compound.

calculated is plotted against the Shore A hardness in Figure 11. The full curve represents the theoretical relation[11] between the Young's modulus and British Standard hardness. B.S. degrees and Shore hardness degrees are approximately equivalent over the useful part of the hardness range. Fairly good agreement is observed between the experimental points and the theoretical curve at hardnesses below 40 but above this value, for the more highly reinforced compounds, the scattering becomes very pronounced. One possible explanation may involve inhomogeneity present in tread compounds. This method is sufficiently accurate for many practical purposes and forms another useful means of determining Young's modulus in addition to supplying the knowledge of puncture strength and depth. The significance of these quan-

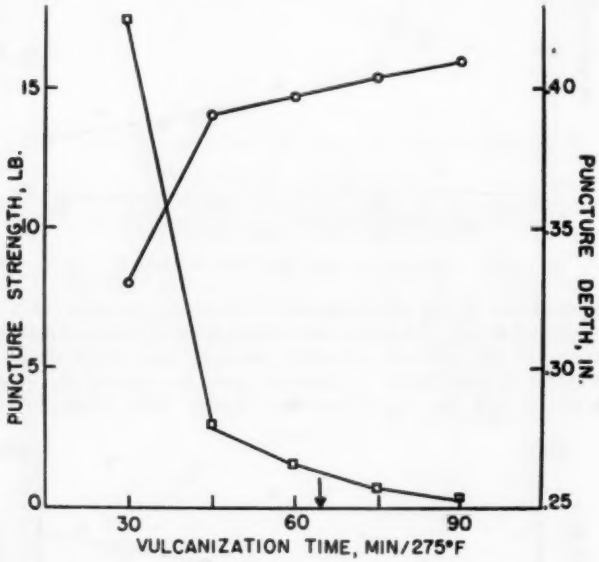

Fig. 16.—OE SBR tread compound.

tities is suggested by the following investigations. The results shown in Figures 12 through 16 were obtained from one inch thick specimens to accommodate the large puncture depth of the soft compounds.

The effect of filler reinforcement on Young's modulus can be sensitively measured by this method. Figure 12 shows the variation of puncture strength and depth with carbon black loading for compound W. The increase in puncture strength and decrease in puncture depth confirms the increase in Young's modulus or hardness with black loading.

The optimum cure in vulcanization is generally judged from tensile, elongation, and 300% modulus data. By means of puncture measurements, the optimum cure can be picked out very simply and readily. Figures 13 through 16 show the variation of puncture strength and depth with variation in cure time at a given temperature for several rubber compounds. An increase in cure time results in an increase in puncture strength and a decrease in puncture

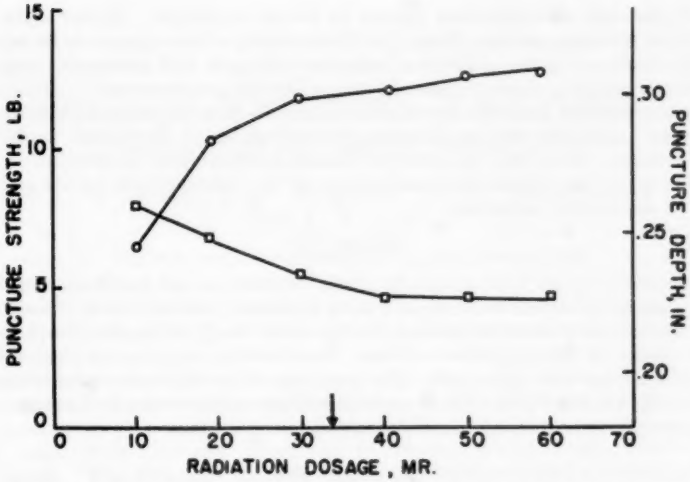

FIG. 17.—Effect of radiation on the puncture strength and the puncture depth for cold SBR tread compound X. ○ puncture strength; □ puncture depth.

depth until at some optimum cure further increase in cure time has little effect on either puncture property, reflecting a fairly constant Young's modulus. The vertical arrow indicates the optimum cure time based on general considerations of tensile, elongation, and 300% modulus data, and with which the puncture method selection agrees fairly well.

A similar study was made on some radiation-cured rubber compounds. The samples containing curatives were molded for five minutes at 275° F and then exposed to given amounts of gamma radiation (Co60). Figure 17 again shows a plot of puncture properties against cure in terms of the radiation dose. The vertical arrow indicates the amount of radiation required for an optimum cure, which is in complete agreement with conclusions drawn from other physical tests.

Of considerable interest is the relationship of the puncture properties to laboratory abrasion resistance and to roadwear rating. We have experience which shows that laboratory abrasion resistance, as measured by ring abrasion, trends with the puncture strength. But it is well known that laboratory abrasion measurements have not correlated well with roadwear ratings. The

TABLE III

COMPARISON OF THE ROADWEAR RATING, PICO ABRASION AND PUNCTURE PRODUCT INDEXES

Compound*	Roadwear* rating	Pico* rating	Relative puncture product
Hot SBR–EPC	90	90 ± 10%	85
NR–EPC	100	100	100
Cold SBR–EPC	110	110 ± 10%	115
Cold SBR–HAF	125	125 ± 10%	125
Cold SBR–SAF	150	150 ± 10%	150

* See Reference (12).

Pico[12] abrasion measurements appear to be an exception. Rather than the puncture strength, we have found that the quantity which appears to be related to the roadwear is the product of puncture strength and puncture depth, or puncture product, which is generally related to the puncture work. Table III gives the relative puncture products for a series of compounds as well as the reported[12] roadwear ratings, showing surprisingly good agreement as do the Pico ratings. However, the puncture test is much simpler to perform.

These studies suggest the potential use of the puncture test for the evaluation of elastomeric materials.

SUMMARY

A detailed study has been made of the indentation and puncture properties of a number of rubber vulcanizates by a puncture method. It is shown that the characteristic relation between the force and depth of penetration, i.e., the two regions of linearity observed in a former study on a log-log plot, can be represented by two equations. The first region, in which the indenter penetrates into the rubber to a depth approximately equal to twice its diameter, can be generally described by Timoshenko's classical relation,

$$F_{\mathrm{I}} = 2.67\ Erd$$

In the second region, an empirically derived equation

$$F_{\mathrm{II}} = 1.34\ Er^{0.5}d^{1.5}$$

holds.

For a given rubber compound, Young's modulus calculated from the second equation is in satisfactory agreement with the modulus obtained from the first.

The puncture strength and the puncture depth are both shown to be dependent upon the compounding variations and they provide useful information about the vulcanizates such as stiffness and cure. Valuable information relating to rubber abrasion and road wear may also result from studies of these two puncture properties.

ACKNOWLEDGMENT

The authors wish to express their thanks to E. F. Devlin and S. D. Gehman for numerous helpful discussions. They are also indebted to H. J. Osterhof and the Goodyear Tire & Rubber Company for permission to publish the work.

REFERENCES

[1] Timoshenko, S., "Theory of Elasticity", McGraw-Hill, New York, 1934, p. 343.
[2] Scott, J. R., *Trans. Inst. Rubber Ind.* 11, 224 (1935).
[3] Scott, J. R., Rubber Chem. & Technol. 21, 939 (1948).
[4] Timoshenko, S., "Theory of Elasticity", McGraw-Hill, New York, 1934, p. 339.
[5] Vickers, H. H. and Robison, S. B., *Proc. Intern. Rubber Conf.*, Washington, D. C., 1939, p. 128.
[6] Livingston, D. I., Yeh, G. S., Rohall, P. and Gehman, S. D., *J. Appl. Polymer Sci.*, in press.
[7] Scott, J. R., Rubber Chem. & Technol. 21, 928 (1948).
[8] Larrick, L., *Rubber Age* 47, 387 (1940); Rubber Chem. & Technol. 13, 969 (1940).
[9] Connant, F. S., Svetlik, J. F. and Juve, A. E., *Rubber World* 137, 856 (1958).
[10] Scott, J. R., Rubber Chem. & Technol. 21, 921 (1948).
[11] B. S. 903, "Methods of Testing Vulcanized Rubber", 1950, p. 114.
[12] Newton, E. B., Grinter, H. W. and Sears, D. S., Rubber Chem. & Technol. 34, 1 (1961).

MOLECULAR ORDERING IN POLYMERS PRECIPITATED FROM SOLUTION *

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Special attention has recently been paid to questions of the molecular ordering of polymers in the condensed state. The degree of molecular ordering determines many physicochemical and mechanical properties of polymers and is therefore practically a very important characteristic of polymeric materials. On the basis of a series of researches it was concluded that the idea regarding amorphous polymers as systems constructed from chains randomly entangled with each other does not correspond to the real model of the structure of polymers. The molecular ordering of polymers is determined not only by the chemical structure and the flexibility of the polymer chains but also by the conditions of preparation of the polymer and may arise even in the amorphous state[1]. An hypothesis has been put forth concerning the bundle structure of polymers, according to which the long molecules of an amorphous polymer may either be collected into bundles in the form of unfolded chains or be turned aside into separate globules. The existence of molecular bundles consisting of unfolded chains arranged in parallel for amorphous polymers was confirmed in one research[2]. In another[3] it was shown by the electron-microscopic method that in the case of certain amorphous polymers one observes an ordered arrangement of the molecular chains leading to the formation of rectilinear parcels. At the expense of regular turnings these parcels may form limited geometrically regular structures. Furthermore, a high degree of ordering of amorphous polymers, close to the order of the crystalline state, was detected in the electronographic (electron diffraction) investigation of several polymers[4].

In the present research we have studied the change of the molecular ordering of polyvinyl chloride, polymethylmethacrylate, and a copolymer of methyl acrylate with methacrylic acid in the process of the heat treatment of samples of these polymers precipitated from solution. We investigated the behavior of polymers in the pressing of samples from reprecipitated and heat-treated material, and also the change of the character of the electronograms (electron diffraction patterns) in the heat treatment of thin films of polyvinyl chloride and polymethylmethacrylate obtained from solutions. For this purpose we used technical polyvinyl chloride of type PF-4 obtained by the suspension method. The molecular weight of the polymer, determined according to the value of the viscosity characteristic in cyclohexanone, was 65,000.

The samples of polymethylmethacrylate were prepared from shavings of a block polymer, which was ground in a mortar and then screened. The fraction that passed through screen 0.25 was taken for the experiment. The samples of the copolymer of methyl methacrylate (85%) with methacrylic acid (15%) were prepared from the block copolymer analogously to the polymethyl-

* Translated from *Vysokomolekulyarnye Soedineniya* 1, No. 9, 1327–1332 (1959).

methacrylate. The samples of the polymers were dried to constant weight in vacuum at 40° and kept in a desiccator over $CaCl_2$.

The reprecipitation of the polymers was carried out as follows: a 1% solution of polyvinyl chloride in freshly rectified cyclohexanone was precipitated with distilled methanol at 5°. The precipitated polymer, after repeated careful washing with methanol, was dried at 40° in vacuum to constant weight. The molecular weight of the reprecipitated polymer did not differ from the molecular weight of the original sample. The polymethylmethacrylate was precipitated from a 1% solution in distilled acetone with the aid of a water-methanol mixture (25% water, 75% methanol) at a temperature of 5°. The precipitated polymer, after repeated washing, was dried at 40° in vacuum to constant weight. The copolymer of methyl methacrylate and methacrylic acid was precipitated with water from a 1% solution in glacial acetic acid. After careful washing the copolymer too was dried in vacuum at 40° to constant weight. All of the reprecipitated polymers, after being dried to constant weight, were then kept under vacuum at 40° for a month.

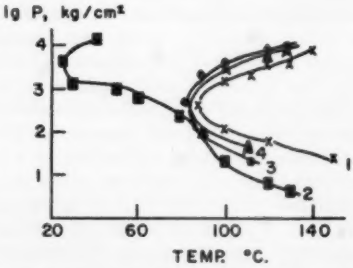

FIG. 1.—Fields of formation of transparent samples in the compression of polyvinyl chloride: *1*, initial polymer; *2*, reprecipitated; *3*, reprecipitated and annealed; *4*, reprecipitated and annealed a second time. Ord.: lg *P* in kg/cm². Abs.: Temperature, ° C.

For the compression of the pulverulent materials we used a cylindrical mold that could be heated. The samples were prepared in the form of tablets 6 mm in diameter and 2–3 mm thick, while the temperature and pressure of the compression were varied within a wide range. The fluctuations of the temperature of the mold did not exceed ±0.5°. The pressing was done on the Schopper universal testing machine. The following conditions of pressing the samples were adopted: a weighed portion of the polymer was placed in the cold mold between two punches (dies) and a certain pressure was given to the upper die. The mold was then quickly heated to the given temperature and kept at that temperature 15 minutes. The mold was then cooled to room temperature, the pressure was relieved, and the sample was extracted from the mold. Furthermore, the transparency of the sample for visible light was estimated visually.

In Figure 1 are shown the pressure-temperature curves for the original unreprecipitated polyvinyl chloride (curve 1) and for the reprecipitated polymer (curve 2). Curve 1 has two branches limiting the field of temperatures and pressures at which one obtains transparent samples: above and below this field one obtains only opaque ones. Thus for each given temperature of compression there are two pressure limits inside which transparent samples can be obtained. The existence of the upper branch[5] was explained by the fact that at sufficiently

high pressures one detects effects of lowering of the mobility of the molecular chain of the polymer. This leads to lowering of the capacity of the grains of material for cohesion (self-adhesion). Thus one can assume that the character of the upper branch is connected in a certain manner with the highly elastic properties of the polymer and reflects its structural characteristics. We were convinced that the change of the highly elastic properties of the polymer by way of plastification, copolymerization, or suturing (joining together) leads to a characteristic change in the position of the upper branch.

Curve 2 of Figure 1, taken for the reprecipitated polymer differs essentially from curve 1. The field confining the conditions for obtaining transparent samples is shifted considerably farther to the left with respect to temperature; the upper branch is situated higher. At the same time it was impossible to take the upper branch completely because of the limited power of the testing machine.

Thus we may conclude that the structure of polyvinyl chloride precipitated from solution differs from the structure of the original polymer.

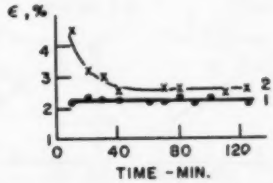

FIG. 2.—Kinetics of the annealing of samples of polyvinyl chloride: *1*, original; *2*, reprecipitated polymer. Ord.: ε in %. Abs.: λ in min.

Curve 3 of Figure 1 was taken for the reprecipitated polymer which had been annealed 4 hours in the pulverulent state at a temperature at 110°. Thus the reprecipitated polymer annealed at a temperature above T_c gives a temperature-pressure curve confining the field of preparation of transparent samples close to the curve of the original polymer. If the reprecipitated and annealed polymer is now reprecipitated again, as described above, one again obtains for it curve 2. Curve 4 was taken for the polymer that had been reprecipitated and annealed again. We repeated the cycle of reprecipitation and annealing for one and the same sample of the polymer five times, and in doing so always observed the reversibility of the effects of reprecipitation and annealing.

Figure 2 shows the kinetics of the annealing of samples pressed from the original (curve 1) and reprecipitated (curve 2) polyvinyl chloride. The samples were compressed at a temperature of 130° and pressure of 250 kg/cm^2 and were subjected to the pressure for 15 minutes. They were annealed in a thermostat of dynamometric weights at a temperature of 100°. The deformation of the samples that developed during an interval of 10 seconds under the action of a constantly acting load of 1.48 kg/cm^2 was determined periodically.

Even though the annealing of the reprecipitated polymer must take place partially even during the compression of the samples, one observes in the additional annealing a marked hardening of the reprecipitated polymer.

In Figure 3*a* are shown the temperature-pressure curves characterizing the field of preparation of transparent samples for polymethylmethacrylate; and in Figure 3*b* for the copolymer of methyl methacrylate and methacrylic acid. As also in the case of polyvinyl chloride, one observes for these polymers a marked

but less sharply expressed difference in the properties of the initial and reprecipitated polymers.

It may be assumed that the initial polymers and those precipitated from solutions differ in their degree of ordering. Those precipitated from solution retain to a known extent their little-ordered state characteristic for solutions of polymers; in the annealing of them there occurs an ordering in the arrangement of the molecular chains by which the chains of the polymer form more perfect bundles. This process is accompanied by a change in the properties of the polymer, which is usually determined as an increase of the rigidity of the chains. At the same time, as we saw above, one observes a lowering of the highly elastic properties of the polymers, which is expressed in a lowered capacity for cohesion and increase of the modulus of elasticity.

It was interesting to trace the change of molecular ordering in the films prepared from the solutions of the polymers, in the process of their annealing, by the electronographic (electron diffraction) method, which is successfully being used now for similar purposes. In the present research such an in-

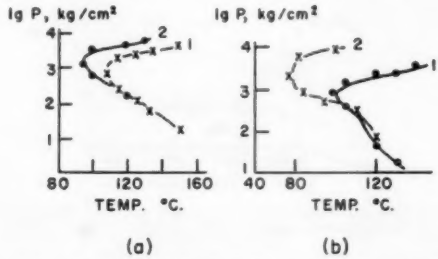

FIG. 3.—Fields of formation of transparent samples in the compression: *a*. of polymethyl methacrylate; *b*. of the copolymer of methyl methacrylate with methacrylic acid. *1*, initial; *2*, reprecipitated copolymer. Ord.: lg *P* in kg/cm². Abs.: Temperature in ° C.

vestigation was conducted for polyvinyl chloride and polymethylmethacrylate. We evaluate the degree of molecular ordering of these polymers according to the curve of relative intensities calculated from the electronograms and normalized with respect to the atomic factor.

The work was carried out on the electronograph of EG construction of the Institute of Crystallography, Academy of Sciences, USSR, with an accelerating voltage of 60 kv. The samples were prepared in the form of thin films by application of several drops of a solution of the polymer in a suitable solvent (1% solutions) on the surface of distilled water and by subsequent catching of them on brass screens. For polyvinyl chloride the solvent was cyclohexanone; for polymethylmethacrylate, acetone served as solvent. After drying, the samples of polymers to be studied were subjected for 2–8 hours to heat treatment in vacuum. The samples of polyvinyl chloride were heated to 100°, those of polymethylmethacrylate to 140°. Furthermore, some samples of both polymers were heated in dibutyl phthalate vapor at 50°.

The resulting electronograms of both polymers each contain three diffuse rings, the intensity of which is uniformly distributed on the circumference, with identity periods for polyvinyl chloride: $d_1 = 5.3$ A, $d_2 = 3.6$ A, $d_3 = 2.2$ A, for polymethylmethacrylate: $d_1 = 6.6$ A, $d_2 = 2.9$ A, $d_3 = 2.1$ A.

Heating of the polyvinyl chloride samples for 2–6 hours at a temperature of 100° did not lead to any visible change of the diffraction picture. An 8-hour

heating under the same conditions causes the appearance of an additional reflection corresponding to a period of identity of 5.05 A. The same effect in the variation of the dispersion picture of polyvinyl chloride is observed after only 2 hours of heating in dibutyl phthalate vapor at 50°.

No marked change is observed in the diffraction picture of polymethylmethacrylate after the heat treatment.

For a more accurate estimation of the change of molecular ordering of the polymers after heat treatment we calculated the curves of dependence of the relative intensities on the angles of dispersion. We judged concerning the degree of molecular ordering according to the heights of the main maximum on the intensity curve lying in the field of the intermolecular distances (5–6 A). The intensity curves were calculated from the electronograms obtained with multiple exposures. The working up of the experimental data was carried out on the basis of application of the law of blackening to the photographing of

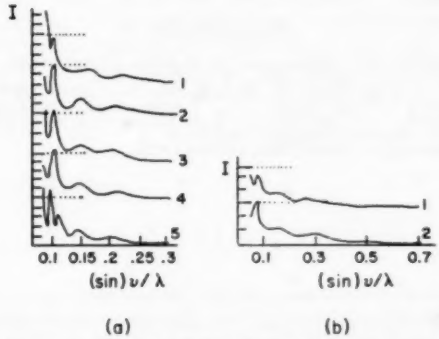

FIG. 4.—Curves of intensities as a function of the angles of dispersion: *a*. for polyvinyl chloride: *1*, original polymer; *2*, *3*, *4*, polymers annealed at 100° 2 hours for *2*, 4 hours for *3*, 6 hours for *4*; *5*, polymer annealed for 2 hours at 50° in dibutyl phthalate vapor; *b*. for polymethylmethacrylate: *1*, initial polymer; *2*, annealed 8 hours at 140°. The values of the relative intensities corresponding to *a*. five and *b*. three units are shown with dotted lines.

the electron beams on photographic plates. For the calculations we constructed blackening curves, from which the mean relative intensities were calculated[6]. For comparison of the curves with each other they were normalized with respect to the atomic factor[7], which was calculated for one molecular grouping being repeated in the chain of the polymer.

In Figure 4*a* are shown the intensity curves for samples of polyvinyl chloride obtained from solution and subjected to heat treatment at 100° for various lengths of time. The intensity curves of polyvinyl chloride contain three maxima, the first of which, lying in the field 5.3 A, ordinarily belongs to the intermolecular distance. In the heating of this polymer, as one sees from the intensity curves, there occurs a gradual ordering in the arrangement of the chain molecules, which is accompanied by an increase of intensity of the main maximum. With longer heating[8] or in dibutyl phthalate vapor one observes the appearance of a new reflection situated at a distance of 5.05 A.

In Figure 4*b* are shown the intensity curves for polymethylmethacrylate obtained from solution and heated 8 hours at 140°. Comparison of these curves shows that the heating in this case also causes the formation of a more

ordered arrangement of the molecules, but to a lesser extent than in the case of polyvinyl chloride.

CONCLUSIONS

1. The variation of the ordering in polyvinyl chloride and polymethylmethacrylate precipitated from solutions in the process of heat treatment was studied.

2. The intensity curves calculated from the electronographic (electron diffraction) data show that the heat treatment leads to the formation of a more ordered arrangement of the chain molecules of these amorphous polymers.

3. The variation of the degree of ordering in these polymers in the heat-treatment process causes a change of the mechanical properties of the polymers and of their capacity for reprocessing.

4. From the data obtained we may conclude that the form of the polymer molecules and their mutual arrangement in the solution differ from those in the condensed state.

REFERENCES

[1] Kargin, V. A. and Markova, G. S., *Doklady Akad. Nauk, SSSR*, **117**, 427 (1957).
[2] Kargin, V. A. and Bakeev, N. F., *Kolloid. Zhur.* **19**, 133 (1957).
[3] Kargin, V. A., Bakeev, N. F. and Vergin, Kh., *Doklady Akad. Nauk, SSSR*, **122**, 97 (1958).
[4] Ermolina, A. V., Markova, G. S. and Kargin, V. A., "Kristallografiya" (Crystallography), **1957**, 101.
[5] Igonin, L. A., Ovchinnikov, Yu. V. and Arzhakov, S. A., *Doklady Akad. Nauk, SSSR*, **120**, 1062 (1958).
[6] Tatarinova, L. I., Trudy Instituta Kristallogr. **1955**, 101.
[7] Vainshtein, B. K., *Doklady Akad. Nauk, SSSR*, **112**, 640 (1957).

STRUCTURE OF FILLED NBR VULCANIZATES BY THE STRETCHING METHOD (MULLINS EFFECT) *

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In work by Mullins[1] and Patrikeev[2, 3] the influence has been demonstrated of previous stretching upon the stress-strain curve of filled vulcanizates. Unfilled rubbers alter their properties insignificantly on stretching. Filled vulcanizates are subject to marked softening during stretching.

This phenomenon has been studied from a qualitative aspect by Blanchard and Parkinson[4, 5, 6, 7]. They started out from the existing equations of Guth, James, Wall, and Flory:

$$F = G\left(\alpha - \frac{1}{\alpha^2}\right) \tag{I}$$

and the equation of Bartenev

$$F = E\left(1 - \frac{1}{\alpha}\right) \tag{II}$$

where F is the force per unit area of original cross-section, α the extension ratio, and G and E constants characterizing the degree of crosslinking of the polymer.

Both equations are valid for non-reinforced rubbers in the range of low and medium extensions.

Since reinforced rubber behaves after heavy previous stretching similarly to a non-reinforced rubber at low elongations, Blanchard and Parkinson made use of the above equations to describe the properties of reinforced rubbers. (In the present paper we used the equation of Blanchard and Parkinson derived by them on the basis of the James-Guth equation.)

They introduced a new term into the equation—the function $F(\alpha)$

$$F(\alpha) = \exp\left[p(\alpha - 1) + \mu(\alpha - 1)^4\right] \tag{III}$$

where p is a constant, equal to 0.31 when we are using Equation I, and μ a coefficient characterizing the deviation in the properties of filled rubbers on stretching in comparison with unfilled.

After conversion the semi-empirical equation of Blanchard and Parkinson has the following form

$$\ln F - f(\alpha) = \ln G + \mu(\alpha - 1)^4 \tag{IV}$$

where

$$f(\alpha) = 0.31(\alpha - 1) + \ln 1.62\left(1 - \frac{1}{\alpha^2}\right) \tag{V}$$

* Translated by R. J. Moseley from *Vysokomolekularnye Soedineniya* 2, 1608–1612 (1960).

Thus, if the rubber under investigation is satisfactorily described by the given equation, then on plotting the graph (on the X axis we plot $(\alpha - 1)^4$ and the Y axis $\ln F - f(\alpha)$) we get a straight line cutting off on the axis of the ordinates a section equal to $\ln G$. The tangent of the angle of slope of the line characterizes the value μ.

What is the physical meaning of the coefficients G and μ? G is a value proportional to the number of all the linkages existing in the vulcanizate, including also the sulfur linkages formed in the process of vulcanization; μ characterizes the degree of interaction of the rubber with the filler.

For unfilled vulcanizates μ is equal to 0. For unfilled vulcanizates with vulcanization accelerators μ has a low value.

The equation given above makes it possible to calculate the force on a transverse linkage.

$$X = \frac{\alpha S}{G^{\frac{1}{3}}} \tag{VI}$$

where α is the extension ratio, S the stress on the original cross-section, and G the coefficient from equation (IV).

It was indicated above that the modulus G is a parameter proportional to the total number of linkages in the vulcanizate. This may be analyzed into two components: G^*, proportional to the number of strong (primary) linkages, which are not destroyed at high stresses; $Gr\,F(x)$ is a parameter which is a function of the previous stressing and characterizing the presence of weak (secondary) linkages, which are destroyed at comparatively low stresses.

Thus the equation

$$G = G^* + Gr \cdot F(x) \tag{VII}$$

serves as a law of the softening of rubbers with active fillers.

In this equation there is introduced the function $F(x)$, which characterizes the number of remaining undestroyed secondary linkages after the application of the stress.

The expression for $F(x)$ has the following form

$$F(x) = \frac{k^3}{4} \int_x^\infty x^{\frac{1}{2}} \cdot e^{-kx^{\frac{1}{2}}}\, dx \tag{VIII}$$

where k is a constant parameter; $F(x)$ alters in the range from 0 to 1.

With low previous stresses $F(x) \rightarrow 1$, with large previous stresses $F(x) \rightarrow 0$.

When $F(x) = 1$, i.e., when no stress is applied to the specimen, the softening formula assumes the form

$$G = G^* + Gr \tag{IX}$$

When $F(x) = 0$, i.e. with very large previous stresses, the second term in the equation is transformed into zero, and we have

$$G = G^* \tag{X}$$

i.e. all the secondary linkages are destroyed.

In constructing the graph we plot on the X axis $F(x)$, and on the Y axis G; equation (VII) gives a straight line, cutting off on the Y axis a section equal to G^*, while the tangent of the angle of slope gives Gr.

Blanchard and Parkinson introduced a semi-empirical equation for natural rubber and the fillers channel gas black and HAF furnace black.

Furthermore they extended their investigations to butadiene-styrene rubber, using various fillers, including mineral fillers such as calcium silicate and magnesium carbonate.

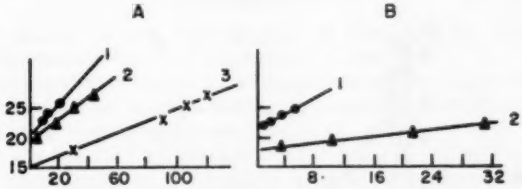

FIG. 1.—Application of the equation $\ln F - f(a) = \ln G + \mu(a - 1)^4$ for a vulcanizate based on SKN-26 containing 28 parts by volume of channel gas black (*a*) and the same amount of aluminum hydroxide (*b*) (S = previous stretching). *a*: *1*—S = 40 kg/sq cm; G = 8.13; $\mu = 2.86 \cdot 10^{-3}$; *2*—S = 50 kg/sq cm; G = 7.5; $\mu = 1.8 \cdot 10^{-3}$; *3*—S = 80 kg/sq cm; G = 6.1; $\mu = 8.9 \cdot 10^{-3}$. *b*: *1*—S = 30 kg/sq cm; G = 8.0; $\mu = 5.5 \cdot 10^{-3}$; *2*—S = 40 kg/sq cm; G = 6.37; $\mu = 1.3 \cdot 10^{-3}$.

Our tests on vulcanized rubbers based on SKN-26 with channel gas black, calcium silicate and aluminum hydroxide showed, as may be seen from Figure 1, *a* and *b*, that the equation given is applicable for the description of the properties of these systems.

For the tests we employed ring-shaped specimens which were subjected to stretching on a tensile tester with automatic recording of the load elongation curves; the rate of stretching was in all cases 200 mm/min, the tests were carried out at +20° C employing previous stresses of from 30 to 120 kg/sq cm.

TABLE 1

ALTERATION IN THE G MODULUS ON INCREASING THE PREVIOUS STRESS

Value of G for a given previous stress, kg/sq cm	Stock composition in parts by volume				
	Natural rubber + 28 of channel gas black	SKN-26 + 28 of channel gas black	SKN-26 + 17 of channel gas black	SKN-26 + 28 of aluminum hydroxide	SKN-26 + 17 of aluminum hydroxide
Before application of stress	9.2	8.8	6.3	8.6	6.0
G 30	9.1	8.5	6.0	8.0	5.5
G 80	7.5	6.1	4.5	4.9	3.0
G 100	7.0	5.5	3.7	3.8	1.45
G 120	6.2	4.15	2.85	2.1	—
Linkages remaining after maximum previous stress, %	67.4	47.0	45.2	24.5	24.4

For each previous stress we took two specimens. The specimen was stretched four times at each previous stressing and was kept under the load for 30 sec.

The data in Table 1 show that for natural rubber with channel black we observe an insignificant reduction in the modulus on increasing the previous stress. Thus with a previous stress of 120 kg/sq cm there remain in the vulcanizate after the fourth stretching 67.4% of the linkages as compared with the original amount. For SKN-26 with channel black with the same dosage the reduction in the modulus is more noticeable. After a stress of 120 kg/sq cm only 47% of the linkages remain. And finally, for SKN-26 with aluminum

hydroxide again 28 parts by volume, we get the greatest reduction in the modulus. After previous stressing, 120 kg/sq cm, there remain only 24.5% of the linkages in the specimen. And for a vulcanizate containing 17 parts by volume of aluminum hydroxide, even at a previous stressing of 100 kg/sq cm only 24.4% linkages are left, while employing previous stressing of 120 kg/sq cm leads to a destruction of the specimen.

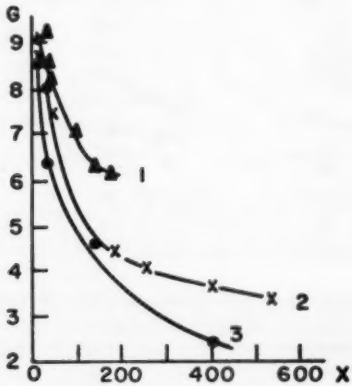

FIG. 2.—Dependence of modulus (G) upon stress concentration on a linkage (x). *1*—Vulcanizate of natural rubber with 28 parts by volume of channel black; *2*—Vulcanizate of SKN-26 with 23 parts by volume of channel black; *3*—Vulcanizate of SKN-26 with 28 parts by volume of aluminum hydroxide.

In Figure 2 we show the relationship between the modulus and stress concentration upon a linkage for three vulcanizates based on natural rubber and SKN-26 with gas channel black and aluminum hydroxide. An analysis of this data shows that with low previous stressing a large number of weak linkages are destroyed, with a low expenditure of energy of rupture: as the previous stressing is increased more and more strong linkages begin to break, and the

TABLE 2

VALUE OF THE COMPONENTS OF THE MODULUS G^* AND Gr FOR VARIOUS RUBBERS

Composition of the stocks parts by volume	G	G^*	Gr
Natural rubber + 28 channel gas black	9.2	5.2	4.0
SKN-26 + 28 channel gas black	8.8	2.8	6.0
SKN-26 + 17 channel gas black	6.3	2.7	3.6
SKN-26 + 28 aluminum hydroxide	8.6	1.2	7.4
SKN-26 + 17 aluminum hydroxide	6.0	0.9	5.1

amount of energy expended increases sharply. After large previous stressing G decreases noticeably, but in every case the value is higher than for unfilled rubbers. Thus, G for SKN-26 without filler is 1.39.

In Table 2 we present the values of the components of the modulus G^* and Gr, characterizing the presence of primary and secondary linkages in the vulcanizates. These values are calculated on the basis of application of Equation (VII).

From Table 2 we see that with vulcanizates of natural rubber with channel black we have the highest values for G^*, i.e. here there are more primary link-

ages. For vulcanizates based on SKN-26 with channel black, and particularly with aluminum hydroxide, the value of G^* decreases, but the value of the modulus Gr increases, which is evidence of the presence of a large amount of secondary linkages, and, consequently, the structure of the vulcanizate is different.

CONCLUSIONS

1. It is possible to use the equation of Blanchard for butadiene-nitrile rubbers with channel black and aluminum hydroxide.

2. It is shown that vulcanizates of butadiene-nitrile rubbers with aluminum hydroxide are subjected to more marked softening on stretching in comparison with vulcanizates containing channel black.

3. Ideas are put forward relating to the ratio of primary and secondary linkages in vulcanizates on the basis of SKN-26 with channel gas black and aluminum hydroxide.

REFERENCES

[1] Mullins, L., *J. Rubber Research* **16**, No. 12, 275 (1947).
[2] Patrikeev, G. A., *Doklady Akad. Nauk SSSR*, **120**, No. 3, 562 (1958).
[3] Patrikeev, G. A., *Zhur. Fiz. Khimii* **33**, No. 9, 2081 (1959).
[4] Blanchard, A. F. and Parkinson, D., *Ind. Eng. Chem.* **44**, No. 4, 799 (1952).
[5] Blanchard, A. F., *J. Polym. Sci.* **14**, 355 (1954).
[6] Blanchard, A. F., *Gummi u. Asbest.* No. 7, 548 (1954).
[7] Blanchard, A. F., *Trans. Inst. Rubber Ind.* **32**, No. 4, 124 (1956).

SWELLING EFFECT OF LIQUIDS ON NBR (NITRILE RUBBER) *

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INTRODUCTION AND REVIEW OF PREVIOUS WORK

While many papers have been published on the behavior of acrylonitrile rubbers in various liquids and the general principles which concern the swelling are well understood, no previous work appears to have been undertaken to obtain an equation relating the volume change with the nitrile content of the rubber. Since such an expression would facilitate the process of predicting the best rubber for a particular application, the effect of various liquids on a series of butadiene-acrylonitrile copolymers was studied with this objective in view.

Many attempts have been made to investigate the different factors which contribute to the swelling of a rubber vulcanizate. Relating the volume change with the level of loading of the compounding ingredients has been reasonably successful. Here Catton and Fraser[4] have shown that the volume change is directly proportional to the percentage, by volume, of the polymer in the compound. Howlett[9] subsequently made a modification to include a factor to cover the extraction of a plasticizer.

Studies to relate the swelling of a particular compound in various liquids with a property of these liquids have, in general, followed two avenues of attack. The fundamental approach has given rise to the concept of the cohesive energy density[7] and solubility parameter[2, 3]. While this has proved extremely useful in obtaining qualitative information, it suffers from the disadvantages that there is no simple method for determining the solubility parameter of polymers and published values[2] tend to vary over a wide range. On the other hand, a practical approach involving the use of either the aniline point[12] or the mixed aniline point[10] has offered a method which, besides having a parameter which is relatively easy to determine, gives a definite indication of the actual volume increase to be expected. However, this method appears limited to a particular class of liquids and does not, at present, have any relation with fundamental ideas.

It will be observed that the above methods have one thing in common, namely, that the behavior of a particular rubber is related to a certain parameter of the various liquids. An alternative route was taken by Saloman[13] who plotted the swelling obtained with a given liquid against the nitrile content for a series of butadiene-acrylonitrile copolymers. It was found that a smooth curve could be drawn through all the points for a given liquid and from this curve useful information could be obtained. Similar work has recently been reported by Fleming[6], who investigated the swelling of different copolymers, as well as blends of copolymers, in oils and fuels.

* Presented before the Division of Rubber Chemistry, ACS, April 20, 1961, Louisville, Kentucky.

EXPERIMENTAL

Butadiene-acrylonitrile copolymers covering the range 0 to 50% of acrylonitrile units were compounded in the formulation:

Polymer	100
Zinc oxide	5
Stearic acid	1
FEF Black	40
Tetramethylthiuram disulfide	3.5

Tensile sheets 6 inch × 6 inch × 0.075 inch were press cured for 30 minutes at 310° F and immersion tests undertaken according to ASTM D 471 for 70 hours at 74° F using 1 inch × 2 inch × 0.075 inch testpieces. The data used in Figures 6, 7 and 8 for various liquids were obtained from published tables[15].

RESULTS AND DISCUSSION

General equation for the swelling curves.—In Figures 1, 2 and 3 the volume change is plotted against the acrylonitrile content (actually the acrylonitrile *unit* constant is plotted in the figures in this paper) and it will be seen that the curves for the different liquids are similar to those obtained by Saloman[13]. Thus an attempt was made to find an equation for these curves. It was found, after a certain amount of trial and error, that the Gaussian type of curve shown in Figure 4 gave a good fit for the points for each liquid when suitable values for the constants α, β and γ were inserted in the equation. These values for a number of solvents are shown in Table 1.

The fact that such curves can be described by a general equation is considered to be a useful advance. However, at this stage it is necessary to carry out swelling tests to determine the value of the constants for a particular liquid.

FIG. 1 SWELLING OF BUTADIENE-ACRYLONITRILE COPOLYMERS IN BLENDS OF ISOOCTANE AND TOLUENE

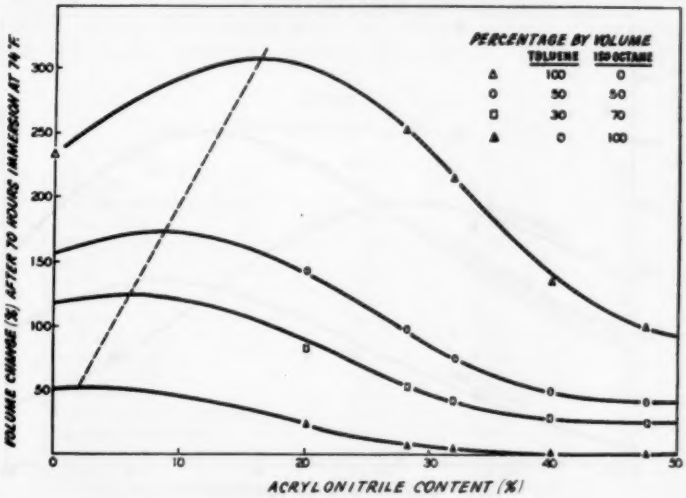
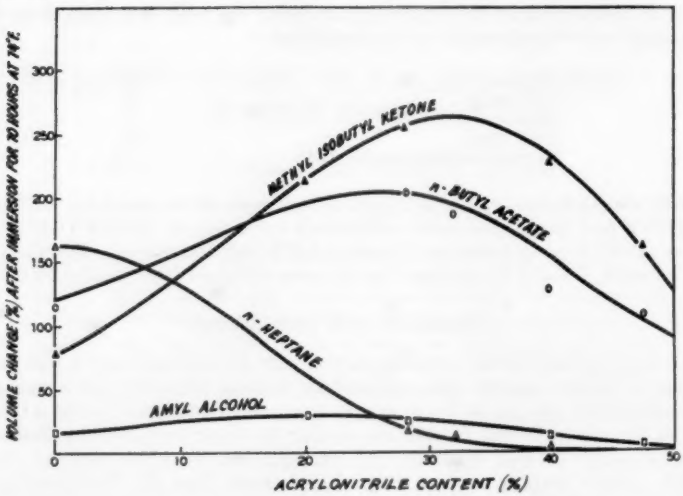


FIG. 2 SWELLING OF BUTADIENE-ACRYLONITRILE COPOLYMERS



It would be extremely helpful if these constants could be obtained from existing physical data, particularly in cases where the liquid is highly flammable, explosive, toxic or just malodorous. Therefore, an attempt was made to relate these constants with various properties of the liquids.

The constants α, β *and* γ.—For a given liquid, the acrylonitrile unit content of the rubber which has a maximum swelling in that liquid is designated by the

FIG. 3 SWELLING OF BUTADIENE-ACRYLONITRILE COPOLYMERS

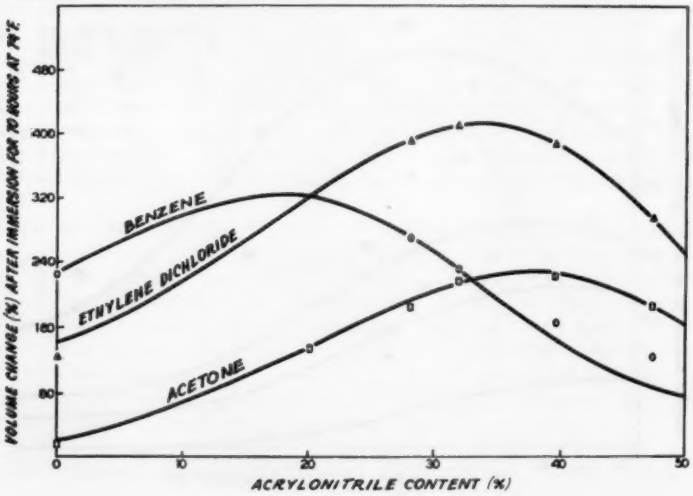
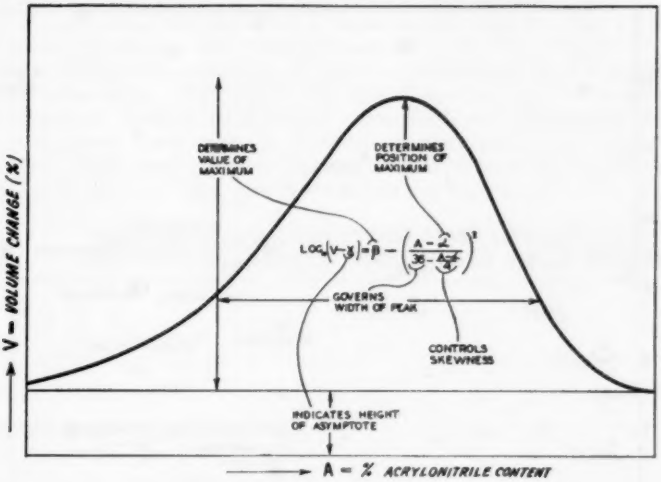


FIG. 4 GENERAL EQUATION OF SWELLING CURVES



constant α. A comparison was first made with the solubility parameter as shown as Figure 5. No definite correlation is evident using the solubility parameter either by itself or in conjunction with the degree of hydrogen bonding in the manner proposed by Burrell[3]. A search was made, therefore, to find other properties of the liquids to which α might be related.

Since Ostwald[11] had used the expression μ^2/ϵ (where μ = dipole moment and ϵ = dielectric constant) as a measure of the solvent power, this was tried but it did not offer any promise. However, it was noticed that there seemed to be some relationship between α and the dielectric constant as shown in Figure 6. This would perhaps be expected since, as stated by Clark[5], "The dielectric constant reflects the molecular configuration and the degree of molecular

TABLE 1

VALUE OF CONSTANTS FOR VARIOUS LIQUIDS

Liquid	α	β	γ
n-Heptane	0	2.21	0
2,2,4-Trimethylpentane	2.0	1.70	0
Cyclohexane	2.5	2.32	0
Carbon tetrachloride	5.5	2.35	44
Fuel B	6.0	2.0	24
Fuel C	9.0	2.12	40
Toluene	16.5	2.35	84
Benzene	18.0	2.42	60
Amyl alcohol	20.0	1.47	0
Butyl acetate	26.0	2.18	52
Butyl acetate	30.0	2.30	0
Chloroform	30.0	2.50	152
Methyl isobutyl ketone	32.0	2.42	0
Ethylene dichloride	34.0	2.57	40
Methyl ethyl ketone	36.0	2.44	0
Acetone	38.0	2.41	−30
N,N-Dimethyl formamide	45.0	2.53	0

FIG. 5 ACRYLONITRILE CONTENT AT MAXIMUM SWELLING & SOLUBILITY PARAMETER

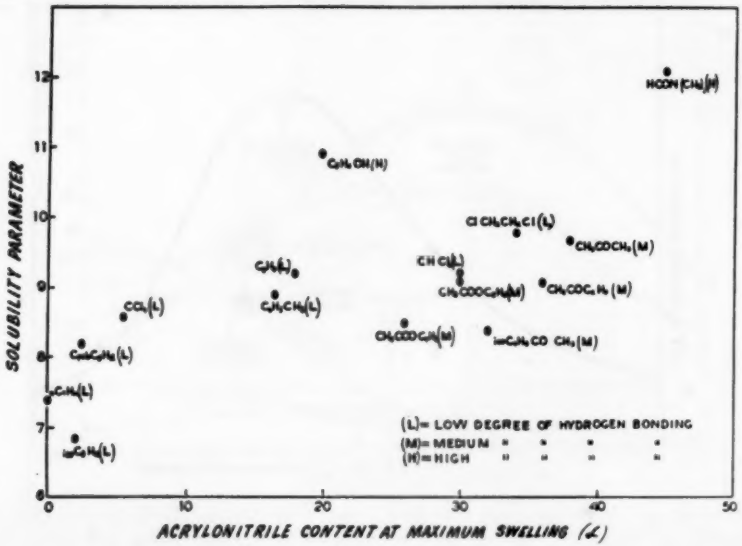
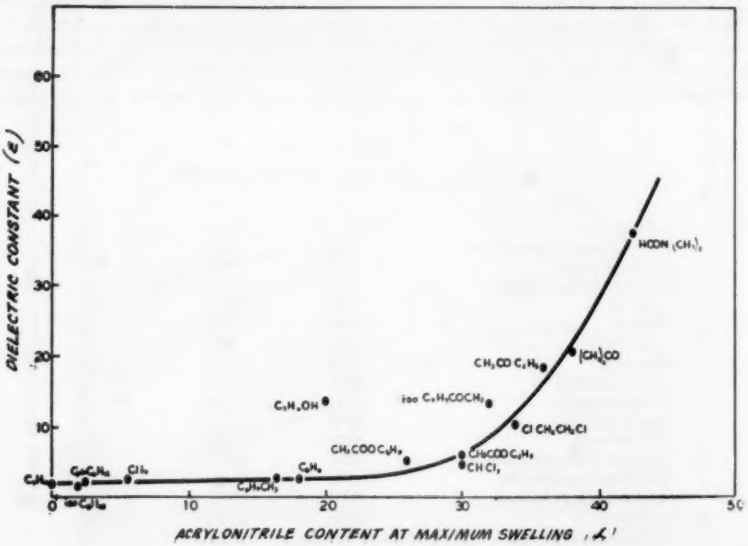


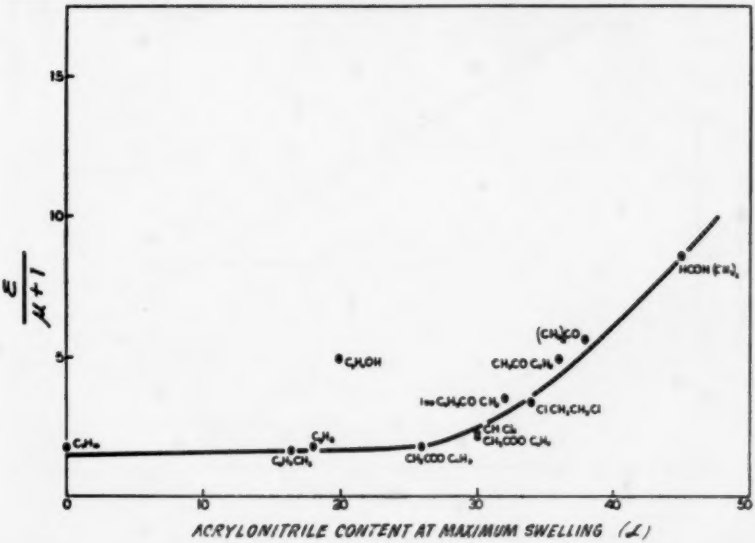
FIG. 6 ACRYLONITRILE CONTENT AT MAXIMUM SWELLING AND DIELECTRIC CONSTANT



polarity. It is therefore, affected by both the position of a substituent in the parent molecule and the electrical nature of the substituent introduced".

An attempt was made to obtain a better relationship by using a function of the dielectric constant and the dipole moment as shown in Figure 7. While this gives a slight improvement for values of α greater than 15, it is not as good at lower values of α. This is probably due to the fact that while saturated hydrocarbons of three or more carbon atoms from an experimental point of view have a zero dipole moment, theoretically they could have small dipole moments[1]. While most of the liquids follow a general trend in Figures 6 and 7, amyl alcohol does not. The reason for this is not known.

FIG.7 ACRYLONITRILE CONTENT AT MAXIMUM SWELLING AND FUNCTION OF DIELECTRIC CONSTANT AND DIPOLE MOMENT



The value of the maximum volume change is controlled by the two constants β and γ. In Figure 8 β is plotted against the molar volume. While there is no simple relationship between the two, it would appear that the value of β tends to increase as the molar volume decreases. While the curves for some liquids, such as cyclohexane and ethyl acetate, could be described by two constants α and β, others, such as chloroform and ethylene chloride, required a third constant γ. This suggested that there were different molecular forces involved for the two groups of liquids.

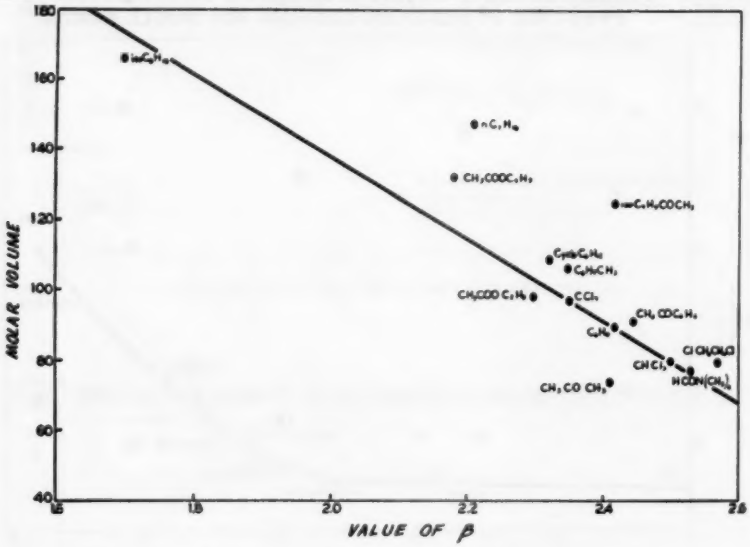
Molecular forces.—According to Staverman[14], molecules can be divided into four classes.

OO Nonpolar molecules, e.g., hydrocarbons and carbon tetrachloride
ON Molecules which have active negative polarity only, e.g., esters, ethers, ketones
PO Molecules which have active positive polarity only, e.g., chloroform

PN Polar molecules which have both positive and negative active polarity, e.g., alcohols, amides and acids.

The main forces between molecules[14] are either (a) London or dispersion forces, or (b) Keesom or electrostatic forces. In the case of the London forces, the attraction between two unlike molecules is nearly the same as that between two like molecules. However, with the Keesom forces there is a marked difference. Attraction occurs between two molecules both of the PN group and also between one from the ON group and one from the PO group.

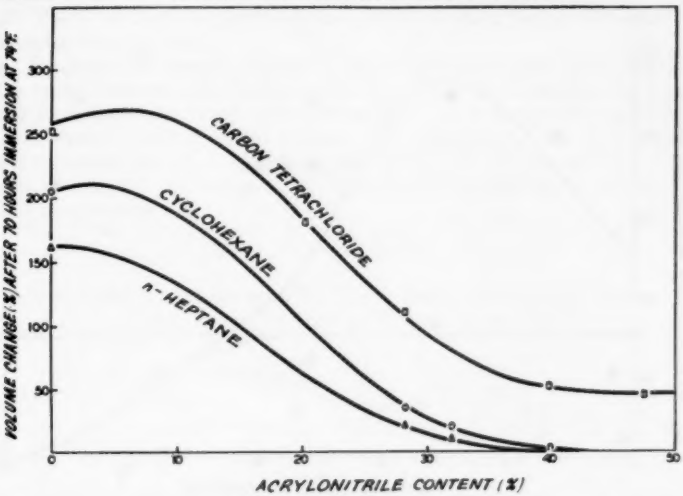
FIG. 8 EFFECT OF MOLAR VOLUME OF LIQUID ON VALUE OF MAXIMUM SWELLING



The curves for the nonpolar liquids *n*-heptane and cyclohexane are shown in Figure 9. While Staverman includes carbon tetrachloride in this group the value of γ would suggest that it should be in another group. Figure 10 gives the curves for methyl ethyl ketone and ethyl acetate which are representative of the ON group.

Liquid molecule with active positive polarity only.—The curve for chloroform is drawn in Figure 11 and this has required a value of γ of 152. Extrapolation of this curve to 100% acrylonitrile unit content would tend to suggest that polyacrylonitrile is swollen by, or is soluble in, chloroform. However, it is unaffected by this solvent. Therefore, it is necessary to consider the molecular forces involved. A possible explanation is that between 0 and approximately 70% polymerized acrylonitrile the copolymers behave as ON molecules and when immersed in liquid molecules of the PO group the electrostatic forces give rise to the value of γ. Beyond the 70% acrylonitrile level, the copolymers change from the ON group to the PN group. Thus these electrostatic forces decrease to zero at 100% acrylonitrile in the manner suggested by the dotted

FIG.9 SWELLING OF BUTADIENE-ACRYLONITRILE COPOLYMERS IN LIQUIDS HAVING NON-POLAR MOLECULES



line on the graph. Since the general type of curve described by α and β appears with liquids of OO and ON groups, as well as the PO group, it would appear that these constants are related to the dispersion forces.

Polar molecules.—Dimethyl formamide was chosen as a representative of this group since it is a solvent for polyacrylonitrile[8]. However, this would not

FIG.10 SWELLING OF BUTADIENE-ACRYLONITRILE COPOLYMERS IN LIQUIDS WITH MOLECULES HAVING NEGATIVE POLARITY ONLY

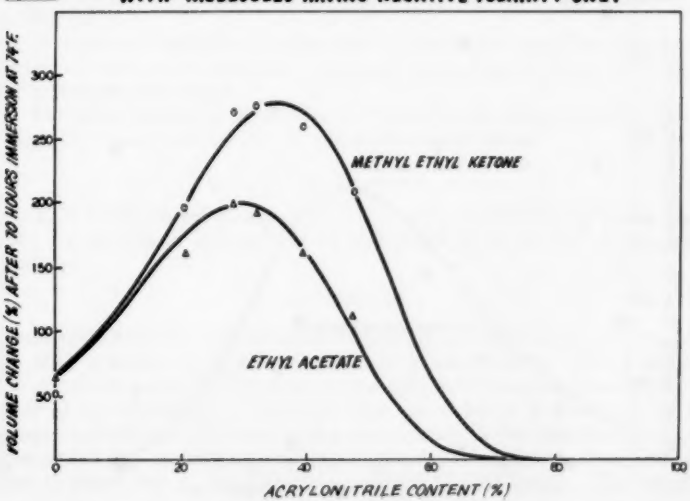
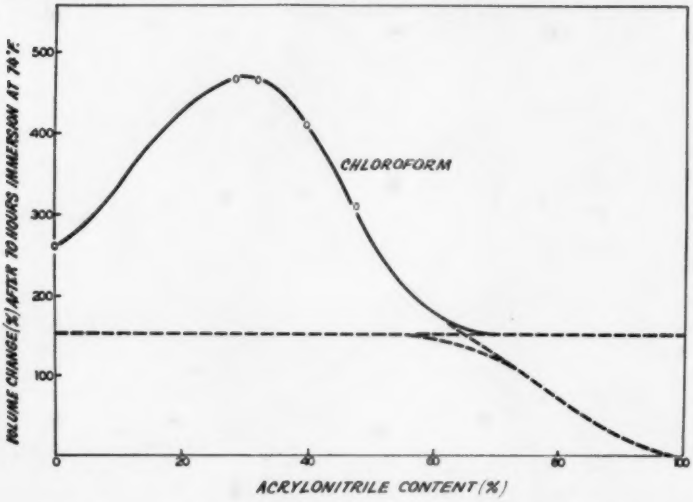
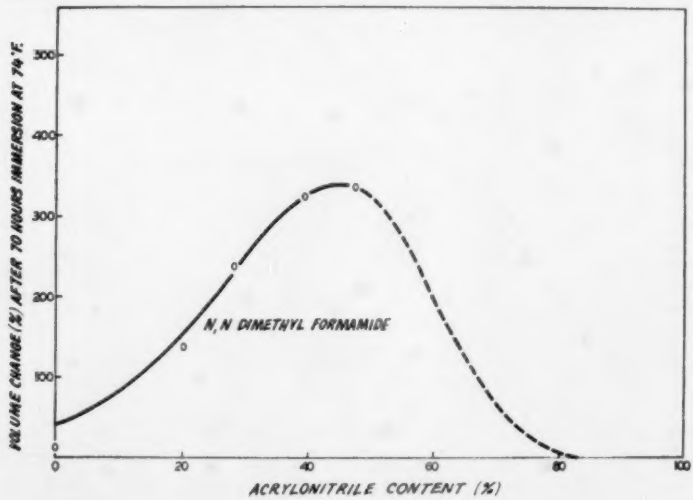


FIG. 11 SWELLING OF BUTADIENE–ACRYLONITRILE COPOLYMERS IN A LIQUID WITH MOLECULES HAVING ACTIVE POSITIVE POLARITY ONLY



be expected from the curve in Figure 12 since if it is extrapolated it reaches zero at about 85% acrylonitrile. Therefore, to explain the behavior of this solvent it is necessary to use similar arguments to those used above for chloroform. Dimethylformamide being of the PN group would not experience any electrostatics forces with copolymers of the ON group so the value of γ would

FIG. 12 SWELLING OF BUTADIENE–ACRYLONITRILE COPOLYMERS IN A LIQUID HAVING BOTH POSITIVE AND NEGATIVE ACTIVE POLARITY



be zero for this range of acrylonitrile. There would, however, be electrostatic forces of attraction between this solvent and copolymers of the PN group, which would include polyacrylonitrile. Thus dimethylformamide would be a solvent for this polymer.

If the argument proposed here is correct, it would thus appear that while in the case of chloroform the dispersion forces and the electrostatic forces are acting over the same range of nitrile content, with dimethylformamide they act at different levels of nitrile content. It would thus seem that γ is not in fact a constant, but is a variable which should be related to two constants similar to α and β. This means that the equation relating to volume change should be rewritten:

$$V = V_L + V_K \tag{1}$$

where V = total volume change (%); V_L = volume change (%) due to London forces; V_K = volume change (%) due to Keesom forces; and

$$V_L = \text{antilog}\left[\beta_L - \left(\frac{A - \alpha_L}{36 - \dfrac{A - \alpha_L}{4}}\right)^2\right] \tag{2}$$

and

$$V_K = f(\alpha_K, \beta_K) \tag{3}$$

where α_L = acrylonitrile content of the rubber which has maximum swelling in that liquid and β_L = logarithm of the value of maximum swelling (to base 10).

CONCLUSIONS

1. For a series of butadiene-acrylonitrile copolymers the swelling by nonpolar solvents is due to the dispersion forces and the volume change in a given liquid can be related to the acrylonitrile unit content by the Gaussian type Equation (2).

2. There is an indication that α_L for a given liquid may be related to the dielectric constant of that liquid while β_L is dependent to some extent on the molar volume of the liquid.

3. For polar liquids it is necessary to include an extra term to take into account the volume change due to the electrostatic forces:

$$V = V_L + V_K$$

where V = total volume change (%); V_L = volume change due to the London forces; V_K = volume change due to the Keesom forces; V_K = function of α_K and β_K.

SUMMARY

Immersion tests in various polar and nonpolar solvents have been undertaken with a range of butadiene-acrylonitrile copolymers. For a particular liquid, it would appear that the volume change can be related to the acrylonitrile content of the rubber by a Gaussian type curve which is described by three constants α, β and γ. The constant α corresponds to the nitrile content of the rubber which has maximum swelling in the liquid and would appear to be related in some way to the dielectric constant of that liquid. The constants

β and γ control the value of maximum swelling. Investigation into the nature of the three constants tends to suggest that α and β are governed by molecular attraction due to the "dispersion forces". On the other hand, γ seems to be connected with the electrostatic forces of attraction and is probably not a constant over the full range of nitrile content, but should be replaced by an expression governed by two other constants. Therefore, to describe the solvent power of a nonpolar solvent, two parameters are needed while four are required for a polar solvent.

ACKNOWLEDGMENTS

Thanks are due to the management of B. F. Goodrich Chemical Company for permission to publish this paper and to various colleagues for their assistance.

REFERENCES

[1] Böttcher, C. J. F., "Theory of Electric Polarization", Elsevier Publishing Co., New York. 1952. p. 329.
[2] Bristow, G. M. and Watson, W. F., *Trans. Faraday Soc.* **54**, 1731 (1958).
[3] Burrell, H., *Official Digest Federation Paint Varnish Production Clubs*, **27**, 726 (1955).
[4] Catton, N. L. and Fraser, D. F., *Ind. Eng. Chem.* **31**, 956 (1939).
[5] Clark, F. M., "The Encyclopedia of Chemistry", ed. Clark, G. L. and Hawly, G. G., Reinhold Publishing Corporation, New York, 1957.
[6] Fleming, C. E., Division of Rubber Chemistry, 79th Meeting, ACS Louisville, Kentucky, April, 1961.
[7] Gee, G., *Trans. Faraday Soc.* **38**, 418 (1942).
[8] Houtz, R. C., *Textile Research J.* **20**, 786 (1950).
[9] Howlett, R. M., *Ind. Eng. Chem.* **37**, 223 (1945).
[10] Meyer, J. and Taylor, J., *Rubber World* **140**, 573 (1959).
[11] Ostwald, W., *J. Oil Colour Chem. Assoc.* **22**, 31 (1939).
[12] Power, P. O. and Billmeyer, B. R., *Ind. Eng. Chem.* **37**, 64 (1945).
[13] Saloman, G., *J. Polymer Sci.* **3**, 173 (1948).
[14] Staverman, A. J., "Adhesion and Adhesives", Chap. 2, ed. De Bruyne, N. A.-Houwink, R., Elsevier Publishing Co., New York. 1951.
[15] Weissberger, A., Proskauer, E. S., Riddick, J. A. and Toope, E. E., "Technique of Organic Chemistry", Vol. VII, Organic Solvents. Interscience Publishers Inc., New York. 1955.

BRANCHING IN BUTADIENE RUBBER *

I. Ya. Poddubnyĭ and E. G. Erenburg

In spite of the considerable interest shown in recent years in the problem of developing a quantitative method for determining the degree of branching in macromolecules, there is presently only a small amount of research in which definite successes have been achieved in this respect[1–5].

Since in most cases the number of branched-chain units which are formed during polymerization and which provide a basis for the formation of long side branches is very small in comparison with the total number of units, the detection of these units by the chemical and spectroscopic methods which are widely used for the determination of the content of side groups in chains is practically impossible at the present time.

Moreover, the presence in the macromolecule of only a few long branches (one branch per several thousand units) results in an alteration in the configuration of the chain in solution, and, as Kuhn[6], Zimm[7], and Tsvetkov[8] have shown, this also results in a noticeable diminution in the dimensions of the molecular aggregate. Consequently, almost all the methods used up to this time for investigating branching are based on the study of the properties of dilute solutions of polymers and the dependence of these polymers on the dimensions and hydrodynamic behavior of the dissolved macromolecules.

A quantitative interpretation of the results is, however, extraordinarily complicated in most cases. Besides the theoretical difficulties involved in establishing a well-defined dependence of these properties on the dimensions of the molecular aggregates in solution, there is also one defect common to all the methods employed; namely, the necessity of comparing the results obtained with the corresponding results for linear polymers of the same chemical structure which themselves are far from being always available.

The most encouraging results have been recently obtained by means of a method in which the intrinsic viscosity of the solutions was investigated. This method is experimentally the simplest and not only permits a direct association to be made between the values thus obtained and the dimensions of the dissolved macromolecules, but also makes it possible, apparently, to obviate the necessity for using linear models[2, 3, 4]. This last consideration is especially important in the study of synthetic rubbers.

1. THEORY OF THE METHOD

In accordance with the contemporary theory of the hydrodynamic properties of macromolecules[9, 10], the intrinsic viscosity of a solution of a polymer can be expressed by the equation

$$[\eta] = \Phi' \frac{(\bar{r}^2)^{\frac{3}{2}}}{M} \tag{1}$$

* Translated from *Vysokomolekularnye Soedineniya* 2, 1625–34 (1960).

where M is the molecular weight of the polymer, $\bar{r}^2$ is the average square of the radius of the molecular aggregate, and Φ' is Flory's universal constant which in elementary expressions does not depend upon the structure or molecular weight of the polymer, or on the solvent, within a high molecular weight region.

For linear polymers this equation can be written in the form

$$[\eta] = KM^{\frac{1}{2}}\alpha^3 \tag{1a}$$

or

$$K = \Phi' \left(\frac{\bar{r}_0^2}{M}\right)^{\frac{3}{2}}$$

α characterizes the change in the linear dimensions of the aggregate as a result of volumetric effects (the symbol θ corresponds to the unperturbed dimensions). Flory's theory leads also to the following relationship between the value $[\eta]$ and the thermodynamic characteristics of the polymer-solvent system[12]:

$$\frac{[\eta]^{\frac{2}{3}}}{M^{\frac{1}{3}}} = K^{\frac{2}{3}} + K^{5/3}{}_2 2\psi_1 C_M \left(1 - \frac{\theta}{T}\right) \frac{M}{[\eta]} \tag{2}$$

In this equation C_M is a constant for the given polymer-solvent system; it is independent of the molecular weight. ψ_1 is the parameter characterizing the entropy of the mixture, and θ is the temperature at which the free energy of the polymer-solvent mixture is equal to the free energy of the formation of an ideal solution. At $T = \theta$ consequently, the free energy of the reaction of the segments of the polymer chain with each other and with the molcules of the solvent is zero. Therefore the coefficient α is equal to 1 at $T = \theta$.

By expanding Flory's theory to the case of branched polymers[2] and designating g as the ratio between the squares of the unperturbed radii of branched ($\bar{r}^2_{\nu 0}$) and linear ($\bar{r}_0^2$) macromolecules, we obtain for branched chains

$$[\eta]_\nu = KM^{\frac{1}{2}}\alpha^3 g^{\frac{3}{2}} \tag{1b}$$

and

$$\frac{[\eta]^{\frac{2}{3}}}{M^{\frac{1}{3}}} = K^{\frac{2}{3}}g + 2C'_M\psi_1 K^{5/3}\left(1 \frac{\theta}{T}\right)\frac{M}{[\eta]}\, g^{\frac{3}{2}} \tag{2a}$$

From these equations it is evident that while for linear chains the dependence $[\eta]^{\frac{2}{3}}/M^{\frac{1}{3}} = f(M/[\eta])$ at $T = \theta$ (in θ-solvent) is linear and parallel to the abscissa, for branched macromolecules this dependence should be a curve with a negative slope, since with an irregular distribution of the branch sites g decreases as the molecular weight increases.

Such a curve is an indication of branching in a polymer. However, since with $M \rightarrow 0$ the number of branch sites in the macromolecule also approaches zero, and consequently $g \rightarrow 1$, then the limiting value of $[\eta]^{\frac{2}{3}}/M^{\frac{1}{3}}$ remains equal to $K^{\frac{2}{3}}$ as before.

Thus, plotting the dependence mentioned above for branched polymers makes it possible to determine the value K, and consequently the unperturbed dimensions of the corresponding linear chains, and g can be found directly from the values for the intrinsic viscosities of solutions of fractions with a known molecular weight in an ideal solvent by the equation,

$$g = \frac{[\eta]^{\frac{2}{3}}}{M^{\frac{1}{3}}K^{\frac{2}{3}}} \tag{3}$$

The calculation of the number of branching sites in the molecule, or the branching density, defined by the ratio of the number of branched units to the total number of units in the molecule, can be found by the equations presented in References 6, 7 and 8. It should, however, be mentioned that a direct transition from Equations (1a) and (2) to Equations (1b) and (2a) is not completely justified. The value for the intrinsic viscosity is determined practically not by the mean square dimensions of the aggregate, but by its hydrodynamically effective dimensions, and the relationship between these parameters (which determine in particular the value of the coefficient Φ') is not the same for branched and linear polymers. Ptitsyn[13, 14] showed that the value of Φ' varies in relation to the deviation of the chain statistics from the Gaussian curve; precisely, Φ' decreases in a good solvent with the increase of volumetric effects, and increases for branched polymers.

A precise theoretical account of this effect presents considerable difficulties in the case of branched polymers, and until recently only an approximate equation, proposed by Stockmayer and Fixman[15], was on hand, which made it possible to associate the value g with the ratio of the squares of the hydrodynamic radii $g[\eta]$, determined from viscosimetric data by Equation 3.

TABLE 1

PROPERTIES OF THE POLYMERS STUDIED

Specimen	Pressure, atm	Temp. of polymerization (temp. of bath), °C	Temp. in polymer °C	Microstructure			Physico-mechanical properties			
				cis-1,4 Link	*trans*-1,4 Link	1,2 Link	Breaking strength, kg/cm²	Ultimate elongation, %	Residual elongation, %	Rebound elasticity, %
SKB-0	0.1	0	17	8	29	63	210	600	18	41
SKB-40	0.1	40	49	8	31	61	135	435	18	32
SKB-60	0.1	60	55	6	30	64	68	347	22	26

This increase in Φ' was observed experimentally for highly branched molecules of dextran[3] and branched polystyrene[16]; the results obtained in Reference (3) agree well with Stockmayer and Fixman's equation.

2. EXPERIMENTAL RESULTS

Using the method described, a study was made of butadiene rubbers obtained by polymerization from the gas phase in the presence of potassium at 0°, 40°, and 60°. Table 1 gives the physico-mechanical properties of the polymers studied, as well as their microstructure; a significant change in the latter can have an effect on the dimensions of the molecular aggregates in solution.

The investigated polymers were divided into fractions of different molecular weight by means of a double fractional precipitation with methanol from dilute benzene solutions. During the fractionation, conditions which insured the obtaining of homogenous fractions were carefully maintained[17].

A control determination of the degree of polydispersity of an arbitrarily chosen fraction (5th fraction of the sample SKB-0) conducted with the aid of an ultracentrifuge, showed that the coefficient of polydispersity characterizing the ratio of the half-width of the sedimentation diagram to the molecular weight at its maximum was approximately 10% for this fraction. The molecular weight of the series of fractions was determined by a visual method. In

this case the determination of $(\pi/c)_0$ was conducted by a linear extrapolation of the value $(\pi/c)^{\frac{1}{2}}$ for an infinite dilution in accordance with the equation $(\pi/c)^{\frac{1}{2}} = (\pi/c)_0^{\frac{1}{2}}(1 + \frac{1}{2}A_2M_c)$ derived from the contemporary statistical theory of dilute solutions of polymers[18]. This method of extrapolation corresponds more precisely to the true nature of the concentration dependence of osmotic pressure in the region of low concentrations than the method employed earlier which involved the linear extrapolation of the value $\pi/c - RTd_1c^2/3M_1d_2^2$ (Here d_1 and d_2 are the densities of the solvent and the polymer and M_1 is the

TABLE 2

MOLECULAR WEIGHT AND INTRINSIC VISCOSITY OF THE FRACTIONS

Sample	Number of fraction	Osmotic molecular weight	Molecular weight	Intrinsic viscosity in benzene at 25°	Intrinsic viscosity in θ-solvent
SKB-0	1	775,000	720,000	4.78	1.30
	1a[1]	1,100,000	1,130,000	6.40	—
	2	—	601,000	4.29	—
	2a	—	980,000	5.80	1.45
	3	—	578,000	4.14	1.27
	4	450,000	480,000	3.74	1.21
	5	—	410,000	3.36	1.13
	6	—	398,000	3.32	—
	7	—	348,000	3.05	1.08
	8	270,000	270,000	2.60	0.97
	8a	382,000	398,000	3.31	—
	9	93,000	95,000	1.37	0.59
	11a	119,000	117,000	1.55	0.64
SKB-40	1	—	—	3.14	—
	2	4,000,000	4,000,000	3.05	—
	3	—	2,600,000	3.00	0.70
	4	1,280,000	1,280,000	2.82	0.72
	5	—	543,000	2.50	0.72
	6	420,000	420,000	2.23	0.71
	7	—	292,000	1.86	0.67
	8	184,000	184,000	1.49	0.61
	9	44,000	44,000	0.68	0.32
SKB-60	1, 2		Large quantity of gel		
	3	—	—	1.92	—
	4	214,000	210,000	1.38	—
	5	—	182,000	1.32	0.50
	6	117,000	108,000	1.00	0.41
	7	70,000	76,000	0.83	0.35
	8	31,000	31,000	0.50	—

[1] The letter *a* designates the second fractionation.

molecular weight of the solvent). In this case it was shown that in work with very poor solvents the results were in practically complete agreement. For all the fractions separated the intrinsic viscosity in benzene was determined at 25° and the dependence of $[\eta]$ on M was plotted for all samples.

The molecular weights of the remaining fractions were calculated from the values for the intrinsic viscosities by the corresponding equations expressing the dependence $(\eta) = f(M)$.

The results of these measurements are presented in Table 2. In the last column are the measurements made of the intrinsic viscosity of the fraction in an ideal solvent $(T = \theta)$.

The ideal solvent for the polymers studied was methyl ethyl ketone at 42°. The θ-temperature was determined on the basis of the dependence of the critical temperature of the complete mixture of the polymer with the solvent (T_c) on the molecular weight of the polymer[10]

$$T_c = \theta \left(1 - \frac{b}{M^{\frac{1}{2}}}\right) \tag{4}$$

where $b = (V_1/\bar{v})^{\frac{1}{2}}/x_1$ (V_1 is the molecular volume of the solvent, $\bar{v}$ is the specific volume of the polymer).

From the equation it follows that θ is the maximum critical temperature of the mixture at $M \rightarrow \infty$. The critical temperature of the mixture is determined by the observation of the temperature at which the fractions are precipitated from solutions of several concentrations close to the theoretical value of the critical concentration.

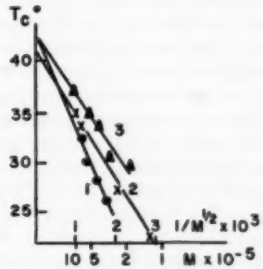


FIG. 1.—Dependence of the critical temperature of precipitation of fractions in methyl ethyl ketone on the molecular weight. *1* and *2*—SKB-0 samples (two fractionations); *3*—SKB-40 sample.

Preliminary experiments showed that the presence of moisture in the solvent causes an extraordinarily sharp change in the temperature of precipitation of the polymer. Thus, the presence of 0.02% water in methyl ethyl ketone increases the temperature of precipitation of butadiene polymers by 1°. Hence, the solvent was carefully dried by the distillation of an azeotrope (containing 11% water) on a fractionating column the fractionating capacity of which was 40 theoretical plates. The results of the measurements of T_c and θ are presented in Figure 1.

3. DETERMINATION OF THE BRANCHING AND DISCUSSION OF RESULTS

In accordance with the theoretical considerations presented above for the determination of the degree of branching of macromolecules on the basis of data on the values for the intrinsic viscosity of fractions in an ideal solvent the dependence $(\eta)^{\frac{1}{2}}/M^{\frac{1}{2}} = (M/[\eta])$ was plotted for the polymers studied.

The results given in Figure 2 indicate the presence of branching in all the specimens studied. Specimens obtained at 0° already display noticeable branching.

It should be mentioned that in the given case due to the curvilinear nature of this dependence for all specimens the finding of the maximum value of $[\eta]^{\frac{1}{2}}/M^{\frac{1}{2}}$ involves well-known difficulties. The value $K^{\frac{1}{2}} = 1.57 \cdot 10^{-2}$ was

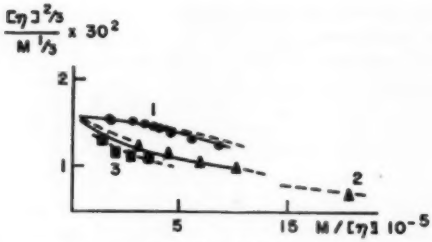


FIG. 2.—Dependence of $[\eta]^{\frac{1}{3}}/M^{\frac{1}{3}}$ on $M/[\eta]$ for the polymers studied. *1*—SKB-0; *2*—SKB-40; *3*—SKB-60.

taken for all three samples; this value was found by the linear extrapolation of the initial portion of the curve for the sample SKB-0. This portion has a very slight slope and consequently the error in such an extrapolation is exceedingly small and has a noticeable effect only on the branching of the very lowest molecular weight fractions. This circumstance, that the curves for the two other samples do not approach sufficiently close to the indicated limit, is explained, in our opinion, by their extremely curvilinear character for highly branched polymers (it should be born in mind that the theoretical value of K is determined by the dimensions of a linear chain of a corresponding chemical structure; the microstructure of the samples studied was the same).

Table 3 gives the values for $g[\eta]$ calculated by Equation 3, the values for g calculated from them[15], and the corresponding densities of branching, determined by Stockmayer and Zimm's equation[7].

In doing the calculations we employed a trifunctional model of branching. Such a model is the most reliable considering the known fact that the propensity to metallization leading to the given type of branching[20] increases in the order Li < Na < K.

TABLE 3

BRANCHING OF THE POLYMERS STUDIED

Sample	Number of fraction	Molecular weight	$g[\eta]$	g	Number of sites in molecule	Density of branching $\rho \cdot 10^3$
SKB-0	2a	980,000	0.822	0.663	6.0	0.33
	1	720,000	0.847	0.700	4.7	0.36
	3	578,000	0.898	0.783	2.9	0.27
	4	480,000	0.924	0.830	2.1	0.24
	5	410,000	0.937	0.855	1.7	0.22
	7	348,000	0.950	0.883	1.3	0.21
	8	269,000	0.962	0.907	0.05	0.21
	11a	117,000	0.968	0.925	0.75	0.34
	9	95,000	0.982	0.955	0.45	0.26
SKB-40	4	1,280,000	0.472	0.300	58.0	2.44
	5	543,000	0.626	0.436	22.0	2.17
	6	420,000	0.675	0.485	16.1	2.09
	7	292,000	0.733	0.550	11.6	2.13
	8	184,000	0.765	0.588	9.3	2.70
	9	44,000	0.848	0.700	4.7	5.90
SKB-60	6	182,000	0.708	0.520	13.5	4.0
	7	108,000	0.740	0.558	11.2	5.6
	8	70,000	0.778	0.605	8.5	6.7

As can be seen from the tables, in the macromolecules of a potassium-butadiene rubber specimen synthesized at 0°, one branching entails on the average about 4000 monomer units ($1/\rho = 3800$) and in macromolecules of high-temperature specimens several hundred units.

The absence of a trimeric structure (gel) in fractions containing $n \cdot 10$ branching sites per molecule, supports the correctness of our trifunctional model.

It is interesting that the branching of the fractions studied remains approximately constant for the fractions of each sample within molecular weights of from 90,000 to 1,000,000, showing no tendency to increase for the highest molecular weight fractions. Thus, in fractionation by the method of fractional precipitation, the fractionation occurs only according to molecular weight even in the case of considerable branching. The influence of branching on the solubility of polymers in the critical region, and consequently, on the fractionating process is not manifest in the system studied. To illustrate this fact the dependence $[\eta]^{\frac{1}{2}}/M^{\frac{1}{2}} = (M/[\eta])$ is plotted in Figure 2 by broken curves; this dependence corresponds to values for g which were calculated at an assumed limit and value of ρ equal to the mean value for each curve.

The above-mentioned considerable increase in the degree of branching of potassium-butadiene rubbers which occurs as the temperature of polymerization increases shows a marked influence on the physico-mechanical properties of the vulcanizates of these rubbers (see Table 1, and Reference (21)).

A specimen obtained at 0°, in which the basic mass of the polymer contains 1–2 branching sites per molecule, is characterized by sufficiently high strength and elastic indexes. Attention is drawn to the fact that, although the very substantial increase in branching observed in the increase of the polymerization temperature to 40° (the number of branching sites in the macromolecule increases to 10–20) leads to a marked impairment in the physico-mechanical indexes, the vulcanizates of these rubbers are nevertheless still technically suitable. At the same time the further, but comparatively less, increase in branching which takes place with a temperature increase to 60° impairs the properties of the polymer to such a degree that it becomes completely unsuitable as a rubber for general purposes. This observation is of a more general character, and apparently indicates the existence of some region in which the physico-mechanical properties of the polymers depend in a comparatively slight degree on their degree of branching.

The results obtained on the effect of the polymerization temperature on the branching of the macromolecules of a potassium-butadiene polymer makes it possible to evaluate the difference between the activation energies of the corresponding reactions of chain growth and branching.

We used in this case an elementary kinetic analysis of the process of branch formation due to metallization which is proposed by Flory[22] and which leads for the general case to the following expression for the density of branching:

$$\rho = -K\left(1 + \frac{1}{n}\ln(1 - n)\right) \tag{4'}$$

where n is the portion of monomer units entering into the polymer chain, and K is a transfer constant.

In the case of a stationary process (which, as Abkin and Medvedev have shown[23], takes place during the gas-phase polymerization of butadiene) where

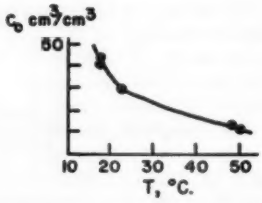


FIG. 3.—Dependence of the solubility of butadiene in SKV rubber on temperature.

the content of the monomer in the polymer ramains constant at all stages of polymerization, Equation 4 can be simplified. At n = constant

$$\rho = K \frac{n}{1 - n} \tag{4a}$$

hence

$$\frac{\rho_{T_1}}{\rho_{T_2}} = e^{-\frac{\Delta E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \frac{\gamma_{T_1}}{\gamma_{T_2}} \tag{5}$$

where $\gamma = n/(1 - n)$.

Thus, the change in the degree of branching with the polymerization temperature, besides the activation energies for the growth and branching reactions, depends on the value of $n(1 - n)$ which is determined by the solubility of the monomer in the polymer.

In this connection we conducted a special series of experiments to determine the solubility of butadiene in SKB rubber under conditions similar to the conditions obtaining in the synthesis of the studied polymers; i.e., at approximately atmospheric pressure and within the temperature interval of 17–50°.

TABLE 4

SOLUBILITY OF BUTADIENE IN SKB RUBBER

Temperature °C	Equilibrium concentration g/g	$\frac{n}{1 - n}$	ρ
17	0.11	9.00	$2.71 \cdot 10^{-4}$
49	0.030	34.70	$2.31 \cdot 10^{-3}$
55	0.024	40.70	$4.00 \cdot 10^{-3}$

The determination of solubility was conducted with the aid of an apparatus designed and kindly presented to us by G. F. Lisochkin and F. D. Belostotskiĭ (VNIISK).

As can be seen from Figure 3, at the temperatures and pressure investigated there is a sharp dependence of solubility on temperature.

The equilibrium values for the concentration of butadiene in the investigated polymer, together with the mean values for the density of branching at the corresponding temperatures, are given in Table 4.

The calculation of the difference between the activation energies, made on the basis of these data using Equation 5 on the assumption that the content of the monomer in the polymer during polymerization is equal to its equilibrium concentration, gives the value $\Delta E \approx 5{,}000$ cal/mol. At the same time, if the

change in the solubility with temperature is disregarded and instead of Equation 5 the following equation is used:

$$\frac{\rho_{T_1}}{\rho_{T_2}} = e^{-\frac{\Delta E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

then on the basis of the data on branching density we obtain the value $\Delta E \approx 13{,}000$ cal/mol.

These values for ΔE are only approximate, since the assumption of the equivalence of the monomer content in the polymer to its equilibrium concentration at a given temperature is only valid when the rate of diffusion of the monomer in the polymer is sufficiently high in relation to the rate of polymerization.

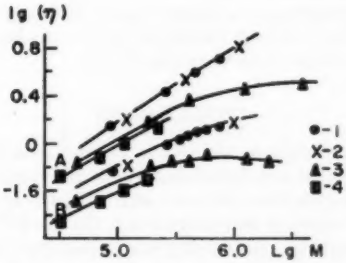


FIG. 4.—Dependence of the intrinsic viscosity of potassium-butadiene rubbers on molecular weight. The *a* curves refer to benzene solutions, the *b* curves to the θ-solvent; *1* and *2*—SKV-0, *3*—SKV-40, *4*—SKV-60.

In the case investigated, in accordance with the work of Abkin and Medvedev mentioned above, this situation does not occur and it is difficult to evaluate the error which this approximation introduces into the determination of ΔE. However, a precise determination of this value was not our task in the given case.

It is of importance that the increase in the branching of the macromolecule with the increase in temperature during the gas phase polymerization of butadiene is to a considerable extent connected with the decrease in the solubility of the monomer in the polymer at high temperatures. Consequently, the branching of the macromolecule can be decreased by means of increasing the gas pressure in the system, compensating thereby the effect of the decrease in the solubility with temperature.

In conclusion we will mention an interesting conclusion resulting from the comparison of the ratios of the intrinsic viscosities for polymers of different degrees of branching in benzene and in an ideal solvent (Figure 4).

As is known[24], the effect of increasing the dimensions of the molecular aggregates resulting from switching from a poor to a good solvent should be greater for denser aggregates of branched molecules.

An analysis of the data in Figure 4, however, shows that the relationship $[\eta]$ for polymers of different degrees of branching in a good solvent such as benzene, remains equal to the corresponding ratio in an ideal solvent for all the ranges of molecular weight investigated and for all polymers studied. Thus the change

in the hydrodynamically effective dimensions of the macromolecule resulting from the switch to a better solvent does not depend upon the degree of branching of the polymer. This observation, can apparently be explained by the fact that the greater increase in the dimensions of the branched macromolecules in a good solvent is approximately compensated for by the difference in the change of the relation between the mean square and hydrodynamic dimensions for branched and linear polymers resulting from the switch to a good solvent

$$\frac{\Phi^b \text{ lin.}}{\Phi^\theta \text{ lin.}} \neq \frac{\Phi_v{}^b}{\Phi_v{}^\theta}$$

This effect has an important methodological significance since it makes it possible to determine the true relation of the hydrodynamically effective dimensions of macromolecules unperturbed by reaction with the solvent, and consequently, in the presence of a linear model, the degree of branching of the corresponding polymers, without having to resort to ideal solvents, which in a number of cases can prove to be very expedient.

CONCLUSIONS

1. By studying the intrinsic viscosities of fractions in an "ideal" solvent, the degree of branching of potassium-butadiene polymers was determined.

It was found that a specimen obtained at 0° was already markedly branched; increasing the temperature of polymerization (to 40–60°) led to the synthesis of highly-branched polymers, containing one branching site per several hundred monomer units.

2. On the basis of quantitative data on the branching of the polymers studied, the difference between the activation energies of the chain growth and branching reactions was calculated for the polymerization of butadiene in the presence of potassium.

At the same time it was found that the increase in the degree of branching of the macromolecules with the increase in temperature in the gas phase polymerization of butadiene was determined not only by the mentioned difference in the activation energies, but also to a considerable extent by the temperature dependence of the solubility of the monomer in the polymer.

3. It was shown that for the investigated system, fractionation of the branched polymers by means of fractional precipitation from dilute solutions yields fractions which differ in molecular weight but not in the degree of branching.

4. It is shown that the relation between the intrinsic viscosities of polymers of a given molecular weight but of a different degree of branching, remains constant in the switch from a good solvent to an ideal solvent.

REFERENCES

[1] Thurmond, C. D. and Zimm, B. H., *J. Polymer Sci.* **8**, 477 (1952).
[2] Wales, M., Marshall, P. A. and Weissberg, S. G., *J. Polymer Sci.*, **10**, 229 (1953).
[3] Senty, F. R., Hellman, N. N. et al., *J. Polymer Sci.* **17**, 527 (1955).
[4] Poddubnyi, I. Ya. and Ehrenburg, E. G., *J. Polymer Sci.* **29**, 605 (1958).
[5] Meyerhoff, G. and Cantow, M., *J. Polymer Sci.* **34**, 503 (1959).
[6] Khun, W. and Khun, H., *Helv. Chem. Acta*, **30**, 1233 (1943).
[7] Zimm, B. H. and Stockmayer, W. H., *J. Chem. Phys.* **17**, 1301 (1949).
[8] Tsvetkov, V. N., *Doklady AN SSR*, **78**, 1123 (1951).
[9] Debye, P. and Bueche, A. M., *J. Chem. Phys.* **16**, 573 (1948).

[10] Kirkwood, J. G. and Riseman, J., *J. Chem. Phys.* **16**, 565 (1948).
[11] Fox, T. C. and Flory, P. J., *J. Phys. Coll. Chem.* **53**, 197 (1949).
[12] Flory, P. J. and Fox, T. G., *J. Amer. Chem. Soc.* **73**, 1904 (1951).
[13] Ptitsyn, O. B. and Einzer, Yu. E., *Zhur. Fiz. Khim.* **32**, 2464 (1958); *Zhur. Tekh. Fiz.* **29**, 1117 (1959).
[14] Ptitsyn, O. B., *Zhur. Tekh. Fiz.* **29**, 75 (1959).
[15] Stockmayer, W. H. and Fixman, M., *Ann. N. Y. Acad. Sci.* **57**, 334 (1953).
[16] Manson, J. and Cragg, L., *J. Polymer Sci.* **33**, 193 (1958).
[17] Bresler, S. E., Poddubnyl, I. Ya. and Frenkel, S. Ya., *Zhur. Tekh. Fiz.* **23**, 1522 (1953).
[18] Fox, T. G., Flory, P. J. and Bueche, A. M., *J. Amer. Chem. Soc.* **73**, 285 (1951).
[19] Flory, P. J., *J. Chem. Phys.* **10**, 51 (1942).
[20] Kocheshkov, K. A. and Talalaeva, T. V., *Sinteticheskie Metody v Oblasti Metalloorganicheskikh Soedineniya*, Moskow, 1949.
[21] Poddubnyl, I. Ya., Reich, V. N., Nazarov, V. G. and Starovoitova, E. I., *Kauchuk i Rezina* **2**, 6 (1958).
[22] Flory, P. J., "Principles of Polymer Chemistry", Cornell University Press, Ithaca, 1953.
[23] Abkin, A. D. and Medvedev, S. S., *Zhur. Fiz. Khim.* **13**, 705 (1939).
[24] Ptitsyn, O. B., *Zhur. Fiz. Khim.* **29**, 396 (1955).

THE MECHANISM WHICH RESTRICTS CHAIN GROWTH IN POLYMERIZATION WITH ALKYLALUMINUM–TITANIUM TETRACHLORIDE COMPLEX CATALYSTS *

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In the production of polymers having a highly regular structure of the molecular chains, catalyst complexes of the Ziegler type are currently in wide use. The development of mechanisms for the separate steps in the catalytic process is of primary significance. This report outlines some results on a study of the mechanisms involved in isoprene polymerization with complexes formed through the interaction of Al (*iso*-$C_4H_9)_3$ and $TiCl_4$; the data were obtained from the sedimentation of the polymers in the ultracentrifuge, in combination with data on the kinetics of polymerization.

We have indicated previously[1] that in isoprene polymerization using the specified catalysts, the growth of the macromolecules proceeds quite rapidly, the time interval between the first appearance of active chains and the termination of reaction being only a few minutes; subsequently there follows an immediate stationary condition. However, with use of the ultracentrifuge we have obtained molecular weight distributions of polymers which are substantially different from the equilibrium distribution expected from present-day kinetic theories of polymerization. They were characterized by relatively low dispersion and, in the main, strongly distorted by high-molecular bands; in most cases, there was practically a complete absence of molecules with a molecular weight less than 200–300 thousand.

Any explanation of the nature of these polymers could be interpreted only on the basis of a new hypothesis, since none of the known mechanisms would lead to such a narrow molecular-weight distribution in a chain termination reaction. It is necessary to postulate a termination mechanism, very responsive to molecular weight (linear) of the chains, and subsequently a rupture of the chains occurring only within sufficiently well-defined molecular-weight limits. Such a mechanism will depend upon the heterogeneity of the polymerization reaction, so, while the chain is growing, one end is attached to the catalytic complex on the catalyst surface. Such an attachment imposes a limit upon the possible configurations of the chain because of restriction in space and movement of segments. Subsequently, rupture of the macromolecules from the catalyst surface is accompanied by an increase in configurational entropy equal to the difference between the logarithms of the statistical sums of the

* Translated by J. R. Robinson from *Doklady Akad. Nauk SSSR*, 134 (1), 117–120 (1960).

free chains in solution and those which are bound to the catalyst surface by their ends.

Assuming a number of possible chain configurations and a quasi-network with co-ordination number γ for free segments and $\gamma/2$ for surface-bound segments, we have established that the "defect" in configurational entropy (ΔS) increases with the number of kinetic segments Z according to the equation:

$$\Delta S = k\sqrt{Z} \tag{1}$$

where k is the Boltzmann constant.

As a basis for discussion, consider at first a model in which the growth of polymer chains takes place by heterocyclic catalytic polymerization. In accordance with this model, the developing polymeric chains have, at all their active ends, alkyl- or halogen alkyl-aluminum. The latter forms, with titanium halide on the catalyst surface, a catalytic complex through crosslinks (or "half bonds"). These bonds are characterized by energies of 10–15 kcal/mole and form, obviously, much less stable links than those of the polymer molecule to the surface. Consequently rupture of such molecules from the catalyst surface will proceed, in all probability, via these weaker bonds, that is rupture will be accompanied by a dissociation of the catalytic complex. This possibility of complex dissociation was first indicated by Natta[2] et al.

Consider separately the reactions of dissociation and re-establishment of the catalytic complex. The velocity constant of a chemical reaction (K) is defined as:

$$K = \frac{kT}{h} e^{-\frac{\Delta U^* - T\Delta S^*}{kT}} \tag{2}$$

where k is the Boltzmann constant, h is Planck's constant, and ΔU^* is the activation energy and ΔS^* is the activation entropy.

The activated state in this monomolecular dissociation reaction retains the structure of the starting complex, that is, the activated macromolecule as in the beginning, is bonded to the catalyst surface. Hence, the activation entropy in this instance, as in most monomolecular reactions, is low and $T\Delta S^* \ll \Delta U^*$, and consequently the velocity constant for the rupture of the polymer chain from the surface of the catalyst, K_1 is of the order of 10^2 to 10^4 per second. The high value of K_1 affirms the fact that the growth of polymeric chains must be interrupted many times because of the dissociations of the active centers at the crosslinks. Throughout this procedure the aluminum remains at the chain ends and growth there can be renewed after re-establishment of the catalyst-complex. The velocity of the re-establishment reaction, where one of the reagents is the polymer molecule, will no longer be determined by the activation energy, which is small in this case, but rather by the entropy of activation and the value of that depends upon the dimensions of the polymer chain. Actually, in this reaction the activated state of all the structures differs little from the final state, that is the transition to the activated form is tied in with the bonding of the polymer ends to the surface. It follows therefore, from Equation (1) that the configurational entropy of the chains is diminished by the amount $\Delta S = k\sqrt{Z}$. The latter, when Z is a significant number, is basically the activation entropy involved in reconstituting the catalytic complex.

From the above it follows that the probability of determining the ratio (X)

of macromolecules in solution to those attached to the catalytic surface $(1 - X)$ may be defined as:

$$\frac{X}{1 - X} = e^{-\frac{\Delta U - T\Delta S}{kT}} \tag{3}$$

where ΔU is the energy which is expended in releasing the polymer molecule from the catalyst surface.

Based upon Equations (1) and (3), we have developed an expression for the relationship in molecular weight distribution within such a polymer sample:

$$\frac{dw}{dM} = \frac{\sqrt{\frac{M}{rM_0}}\, e^{-\frac{\Delta U}{kT} + \sqrt{\frac{M}{rM_0}}}}{2\left(1 + e^{-\frac{\Delta U}{kT} + \sqrt{\frac{M}{rM_0}}}\right)^2} \tag{4}$$

where w is the weight factor, r is the number of monomeric members in the kinetic segments and M_0 is the molecular weight of the monomer.

This distribution is characterized by curves, of which the coefficient of dispersion is defined by the equation:

$$\frac{\delta M}{M} \simeq \frac{3kT}{\Delta U} \tag{5}$$

Thus the dispersion curves showing molecular weight spread are established on the energy of the bonds connecting the polymer molecules with the surface of the catalyst. When the magnitude of $\Delta U \simeq 10$–15 kcal/mole then the coefficient of molecular weight dispersion approximate a value of 0.1, that is, it is very low. Consequently the proposal of a mechanism limiting molecular weights of chains by polymerizing with a heterogeneous catalyst-complex, brings about the possibility of producing polymers having a very narrow molecular weight range. We have actually obtained such polymers through

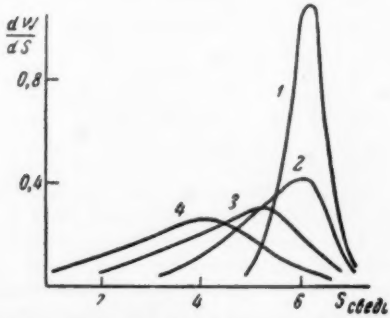

FIG. 1.—Molecular weight distribution of polyisoprene. *1*—Al (*iso*-C_4H_9)$_3$:$TiCl_4$ = 1:1. Catalyst seasoned for 24 hours; polymerization temperature 0°. *2*—Fresh catalyst Al (*iso*-C_4H_9)$_3$:$TiCl_4$ = 1:1. *3*—Al (*iso*-C_4H_9)$_3$:$TiCl_4$ = 1:1 + 0.5 (*iso*-C_4H_9)$_3$ (with the monomer). *4*—Al (*iso*-C_4H_9)$_3$:$TiCl_4$ = 1:1 + Al (*iso*-C_4H_9)$_3$. Curves 2–4: temperature of polymerization was 30°. w is the weight factor and S the sedimentation constant.

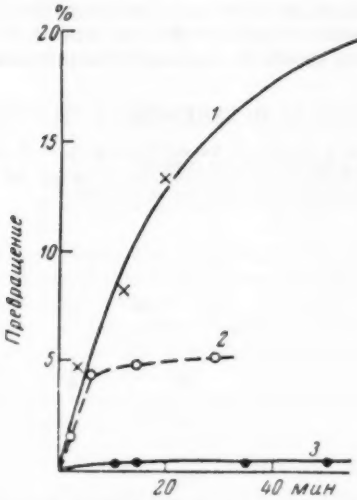

FIG. 2.—Curves of kinetics of polymerization of isoprene at 30° C. *1*—Al (*iso*-C_4H_9)$_3$:$TiCl_4$ = 1:1. *2*—The same + 0.5 Al (*iso*-C_4H_9)$_3$ with monomer. *3*—Al (*iso*-C_4H_9)$_3$:$TiCl_4$ = 1.5:1. The ordinate is conversion and the abscissa time in minutes.

polymerizing isoprene as a pure monomer at low temperature (0° C) by using a catalyst-complex (in ratio 1:1) held over a 24 hour period. In Figure 1 the calculated coefficient of dispersion dw/dS, (where S is the sedimentation constant in octane when the concentration of the polymer is 2 mg/ml) was 0.1, while in the actual curve it proves to be $\simeq 0.15$.

Thus the catalyst-complexes differ not only in stereospecificity but also in providing, under defined conditions, the production of polymers with high steric homogeneity. The above mechanism appears to be operative, however, only in those cases where the growth of the macromolecules is not interrupted. One factor which occasions "premature" rupture of the molecular chains is the presence in the catalyst of free tri-*iso*butylaluminum[3]. We verified this fact in special tests in which a previously prepared catalyst-complex (ratio 1:1) was introduced into a monomer containing a measured quantity of (*iso*-C_4H_9)$_3$ Al. At the beginning of the polymerization, while an excess of the (*iso*-C_4H_9)$_3$ Al existed, the polymerization velocity was maintained at about normal, (Figure 2) but the molecular weight distribution of the polymer was sharply displaced towards the lower region (Figure 1, curves *3* and *4*). This affirms that the termination mechanism operative in those chains not bonded to the organoaluminum becomes one of reaction transfer, that is, proceeds by regenerative active centers. Obviously then, if freshly prepared catalyst, in ratio of 1:1, still contains some free (*iso*-C_4H_9)$_3$ Al, the resulting polymer will contain a large amount of low-molecular weight fractions; the same catalyst, after seasoning for 24 hours, causes formation of much higher molecular weights (Figure 1, curves *1* and *2*).

These results permit the conclusion that in catalytic-complex polymerization a rupture of chains by a transfer mechanism occurs only in particular cases

where free organoaluminum, or other compounds capable of transfer reactions, are present. In the absence of such components rupture of the chains proceeds according to mechanisms specific to heterogeneous polymerization as outlined above.

REFERENCES

[1] Bresler, S. E., Mosevitskiĭ, M. I., Poddubnyĭ, Ya. and Chesnokova, N. N., *Zhur. Tech. Fiz.* **28**, 2487 (1958); Rubber Chem. & Technol. **33**, 689 (1960).
[2] Natta, G. and Pasquon, J., *Atti Accad. Naz. Lincei Rendi Sci. fis.* **26** (45), 617 (1959).
[3] Natta, G., Posquon, J. and Giachetti, E., *Chim. et Ind.* **40**, 97 (1958).

SYNTHESIS OF ISOPRENE TAGGED WITH C^{14} *

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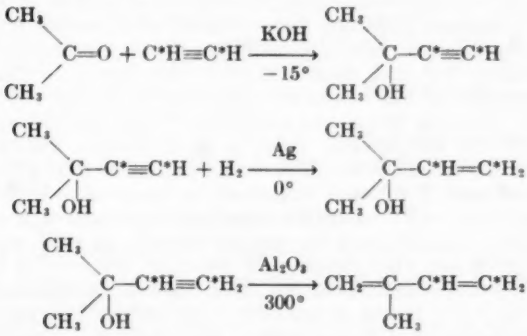
For a study of the mechanism of catalysis of polymerization of diene hydrocarbons and also for investigation of the process of catalysis of copolymerization the following hydrocarbons tagged with C^{14} were synthesized: benzene[1], toluene[1] and isoprene. The simplest ordinary methods possible were used for these syntheses to obtain pure active preparations in good yields from starting materials containing radioactive carbon.

Isoprene-C^{14} was synthesized according to the method of A. E. Favorskiĭ[2] in three steps according to the scheme:



I

II

III

In distinction from the method of Favorskiĭ, 2-methyl-3-butyn-2-ol was obtained in the presence of excess acetone.

Hydrogenation of 2-methyl-3-butyn-2-ol was conducted electrolytically under conditions worked out by A. I. Lebedev[3].

The resulting vinylcarbinol-C^{14} was transformed into isoprene by dehydration over active aluminum oxide.

EXPERIMENTAL

Preparation of acetylene-C^{14}.—Acetylene-C^{14} was obtained according to the scheme: $BaC^*O_3 \rightarrow Ba^*C_2 \rightarrow C_2{}^*H_2$, barium carbide being obtained according to the method of N. P. Cayer, B. V. Kliminos and G. V. Isogoolyan[4] and acetylene by decomposition of the carbide by water in the apparatus suggested by Cheronis[5] and modified by us in the detail arrangement of traps for condensation of acetylene-C^{14}—A in Figure 1.

The yield of acetylene was determined manometrically and amounted to 72–80% calculated on the barium carbonate.

* Translated by E. C. Gregg, Jr. from "Isotopes and Radiation in Chemistry", Acad. Sci. USSR Press, Moscow (1958), pp. 358–360.

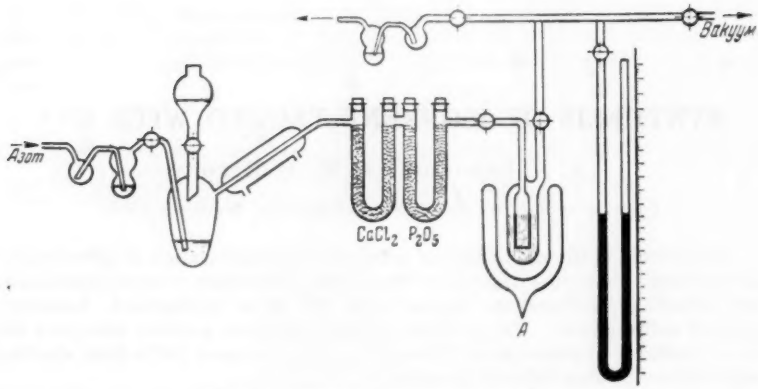


FIG. 1.—Apparatus for preparation of acetylene.

Preparation of 2-methyl-3-butyn-2-ol-C^{14}.—The condensation of acetylene and acetone by potassium hydroxide was conducted in apparatus B shown in Figure 2. Into the reaction vessel (capacity 150 ml) were introduced powdered potassium hydroxide (9 g) and absolute diethyl ether (60 ml). The air was pumped from apparatus B and radioactive acetylene (20–30 ml) was admitted from the trap A. Acetone (2.5 g) and acetylene-C^{12} (500–600 ml) were introduced alternately into the reaction vessel in small portions during definite intervals of time (20–30 minutes). The reaction mixture during the course of the entire experiment (7–8 hours) was stirred by means of an electric motor and was maintained at $-15°$. After the experiment was finished, the reaction mixture was worked up with twice the amount of water as alkali used. The ether layer was dried and, after distilling off the ether, the residual 2-methyl-3-butyn-2-ol-C^{14} was distilled from the flask with a dephlegmator. For complete removal of the tagged preparation from remnants in the distilling flask 2-methyl-3-butyn-2-ol-C^{12} was added and distilled. This operation was repeated 3 to 4 times until radioactive carbon, C^{14}, was absent in the

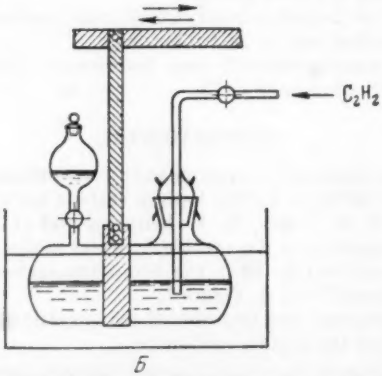


FIG. 2.—Apparatus for condensation of acetylene with acetone and potassium hydroxide.

distillate. The yield of carbinol as measured by the activity due to the introduction of acetylene-C^{14} is 55–70%.

Preparation of 2-methyl-3-buten-2-ol-C^{14}.—Electrolytic hydrogenation was conducted at 0° in an electrolytic cell (capacity 200 ml) in 5% alkali solution without division of anode and cathode compartments. Initial concentration of carbinol in the solution is 7–12%. The cathode used was silver plated copper sheets, the anode was nickel. The current density is 2 amps/dm^2. The completion of hydrogenation was determined according to negative reaction of the triple bond with an ammoniacal solution of silver. The electrolyte was distilled into three parts and 2-methyl-3-buten-2-ol-C^{14} was isolated from it by the potassium salting out process. The carbinol was dried by anhydrous potassium carbonate and was distilled from the vessel with a dephlegmator with consecutive addition of small portions of the carbinol-C^{12}. The yield of carbinol as measured by activity comprises 87% based on the 2-methyl-3-butyn-2-ol-C^{14}.

Preparation of isoprene-C^{14}.—Dehydration of the vinyl carbinol-C^{14} was effected over active aluminum oxide (size of grains 3–4 mm) at 300° in a quartz tube with a diameter of 1.5 cm and a length of 4.5 cm. The vinyl carbinol was added at a rate of 0.4 ml/minute. Products of reaction were collected in a trap immersed in a freezing mixture. The hydrocarbon layer was dried and distilled. There was collected a fraction with a boiling point 34–35°. The yield of isoprene-C^{14} due to the initial acetylene-C^{14} is about 50%.

The measurement of radioactivity of the compounds prepared was made in a type B mounting with a wood counter.

The methods of synthesis were worked out first with nonradioactive materials. Physical-chemical constants of the compounds prepared corresponded to literature data.

REFERENCES

[1] Korotkov, A. A. and Mitsengendler, S. P., *Izvestia Akad. Nauk SSSR, Otdel. Khim.* No. 12, 1508, 1509 (1956).
[2] Favorskii, A. E., *J. Russ. Phys.-Chem. Soc.* **32**, 659 (1900); *ibid.* **37**, 643 (1905). A. E. Favorskii. Workers of the session for organic chemistry of the Academy of Science of USSR (1939).
[3] Lebedev, A. I., *Zhur. Obshchei Chem.* **18**, 1161 (1948).
[4] Cayer, H. P., Klimenok, B. V. and Isagulyants, G. V., *Doklady Akad. Nauk.* **85**, 1029 (1952).
[5] Cheronis, N., "Micro and Semimicromethods". Interscience Publ., N. Y., 1954, p. 396.

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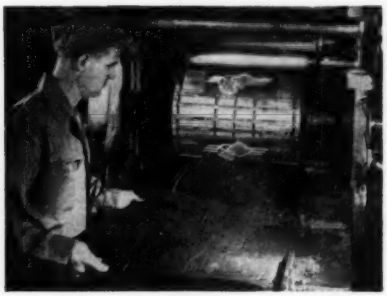

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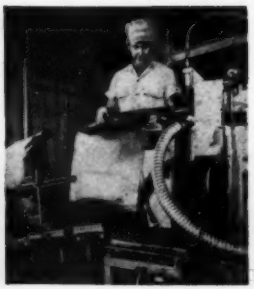

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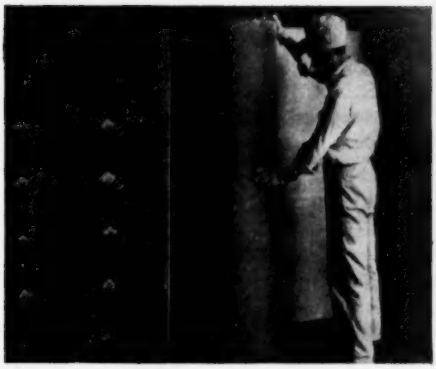

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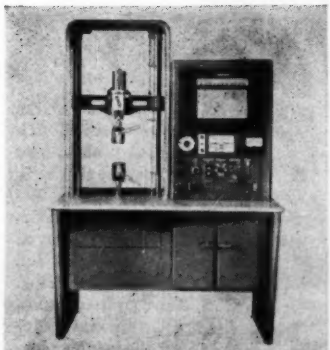

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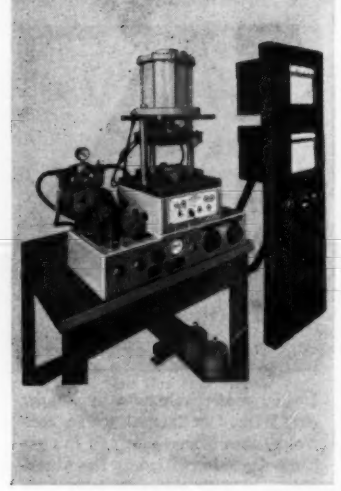

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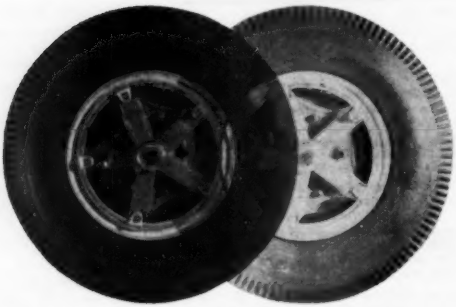

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